Journal of the Institute of Petroleum

VOL. 43 OCTOBER 1957 No. 406

CONTENTS

273 **Petter Engine Tests of Diesel Lubricating Oils**
By R. Tourret and R. W. Bale

282 **The Measurement of the Surface Tension and Interfacial Tension of Insulating Oils**
By L. Massey, N. N. Murty, and C. N. Thompson

287 **Obituary: R. M. Johnson**

288 **The Separation of Mixtures of Biphenyl, *cyclo*Hexylbenzene, and Bi*cyclo*hexyl by Vapour-phase Chromatography**
By W. J. Hendriks, R. M. Soemantri, and H. I. Waterman

292 **Report of IP Carbon Residue Panel**

Abstracts 1642–1910

Book Reviews

Additions to the Library

PRICE 10s 0D A COPY OR £4-14-6 YEARLY *POST FREE*

Published by the Institute of Petroleum 26 Portland Place London W1

Printed in Great Britain by Richard Clay and Company Ltd Bungay Suffolk

COUNCIL, 1957–58

President

The Rt. Hon. Lord Geddes

Past-Presidents

Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc.
T. Dewhurst, A.R.C.S.
A. E. Dunstan, D.Sc., F.R.I.C.
E. A. Evans, M.I.Mech.E., F.R.I.C.
F. H. Garner, O.B.E., Ph.D., F.R.I.C.
Sir H. S. Gibson, C.B.E., M.A., M.I.Mech.E.
C. A. P. Southwell, C.B.E., M.C., B.Sc.

Vice-Presidents

E. B. Evans, M.Sc., Ph.D., F.R.I.C.
A. C. Hartley, C.B.E., F.C.G.I., B.Sc.(Eng.), M.I.C.E., M.I.Mech.E.
E. Le Q. Herbert, B.Sc., F.R.I.C., M.I.Chem.E.
H. Hyams
R. B. Southall, C.B.E.
E. J. Sturgess, C.B.E., B.Sc.

Members of Council

W. S. Ault, B.A.
V. Biske, B.Sc., LL.M., F.R.I.C.
E. J. Dunstan, M.Sc., M.I.Chem.E.
F. L. Garton, M.A., B.Sc.
A. J. Goodfellow, B.Sc., A.R.I.C.
N. W. Grey, M.I.Chem.E., M.E.I.C.
M. E. Hubbard, B.A., M.I.Mech.E.
E. C. Masterson, B.Sc.
T. W. Mathias, O.B.E., M.A.
F. Morton, Ph.D., D.Sc., F.R.I.C.
J. S. Parker, M.A., B.Sc.
K. E. W. Ridler, Ph.D.
A. J. Ruthven-Murray, C.M.G., M.A., B.Sc.
D. L. Samuel, B.Sc., A.R.I.C.
G. H. Smith, Ph.D.
A. R. Stark, B.Sc., A.R.I.C.
W. H. Thomas, A.R.S.M., F.R.I.C.
G. H. Thornley, M.Sc.
A. T. Wilford, B.Sc., F.R.I.C.
C. G. Williams, D.Sc., M.I.Mech.E., F.R.Ae.S.
C. S. Windebank, B.Sc., M.S.

Ex-Officio

S. A. Berridge, B.Sc.
A. S. Brooman, B.Sc.
A. H. Chatting
J. C. Jewell, B.Sc., A.R.C.S., A.R.I.C.
L. S. Thornes, B.Sc., Ph.D., D.I.C., M.R.C.S.
J. C. Wood-Mallock

Honorary Secretary

C. Chilvers, B.Sc., F.R.I.C.

Honorary Treasurer

G. H. Coxon

General Secretary

D. A. Hough, T.D., F.I.A.C.

Honorary Editor

E. B. Evans, M.Sc., Ph.D., F.R.I.C.

Honorary Associate Editor

D. L. Samuel, B.Sc., A.R.I.C.

Editor

George Sell

Honorary Secretaries of Branches

Bahrein Branch: H. G. Babbage, c/o Bahrein Petroleum Co. Ltd., Awali, Bahrein, Persian Gulf.

Essex Branch: E. Bowes, A.R.I.C., Mobil Oil Co. Ltd., Central Laboratories, Coryton, Essex.

Fawley Branch: S. A. Berridge, B.Sc., c/o Esso Petroleum Co. Ltd., Fawley, Southampton.

Kuwait Branch: R. J. L. Stephens, c/o Kuwait Oil Co. Ltd., Ahmadi, Kuwait.

London Branch: S. C. Price, F.C.S., c/o Jet Lube Ltd., 26 Caxton Street, London, S.W.1.

Northern Branch: H. Kaye, B.Sc., A.M.I.Chem.E., c/o Manchester Oil Refinery Ltd., Twining Road, Trafford Park, Manchester 17.

Scottish Branch: W. M. Stirling, A.H-W.C., A.M.I.E.E., Scottish Oils Ltd., Middleton Hall, Uphall, Broxburn, W. Lothian.

South-Eastern Branch: J. R. Moore, Fisher Governor Co. Ltd., Airport Works, Rochester, Kent.

South Wales Branch: D. J. Lewis, BP Refinery (Llandarcy) Ltd., Llandarcy, Glam.

Stanlow Branch: A. S. Brooman, B.Sc., 11 Grange Crescent, Hooton, Wirral, Cheshire.

Trinidad Branch: G. Hillier, Apex (Trinidad) Oilfields Ltd., Fyzabad, Trinidad, B.W.I.

PETTER ENGINE TESTS OF DIESEL LUBRICATING OILS*

By R. TOURRET† (Associate Fellow) and R. W. BALE† (Associate Fellow)

INTRODUCTION

DURING the last two decades the Caterpillar 1.A oil test engine has become [1] the principal unit on which the performance of a diesel engine lubricating oil is rated, in regard to such factors as carbon and lacquer deposit formation, ring sticking, wear, etc. It is a sound engine mechanically and it gives good results, but it suffers from disadvantages in that it takes a long time to test an oil (three or four weeks, depending on whether or not intermediate inspections are required) and that spares are expensive and often involve dollar expenditure. The initial cost is high and also involves dollar expenditure. Several attempts have been made to supplement or replace the Caterpillar engine by a shorter test on a cheaper engine. One of the engines which in the last few years has come to the fore as a possible Caterpillar replacement is the Petter A.V.1 engine, using the AT/4 test method.[2] Six Petter A.V.1 engines were installed at the Admiralty Oil Laboratory (A.O.L.).

Admiralty storage of diesel lubricants is unusual in that, of necessity, large stocks have to be held in various depots throughout the world under greatly differing atmospheric conditions. This produces a quality control problem not encountered to any great extent elsewhere, that of confirming from time to time that the condition of such stocks has not deteriorated. It is well known that it has not yet been possible to devise chemical or physical tests which satisfactorily predict the service performance of such oils in engines. Accordingly, some form of engine test was essential. It was hoped that the use of the Petter A.V.1 engine for such a test might obviate the use of the long and expensive Caterpillar procedure.

This paper considers the installation of the Petter A.V.1 engines at A.O.L., the repeatability and reproducibility of results obtained from them, and the possible relationship between results obtained from oils tested on the Petter engine and on the Caterpillar engine.

APPARATUS

The Petter engine and one type of installation have already been described elsewhere,[2] and so a comparatively brief description will suffice here.

The six engines used in the tests undertaken at A.O.L. were Petter A.V.1 single-cylinder, four-stroke, compression-ignition engines close-coupled to Heenan & Froude DPX4 dynamometers (Fig 1). The engines and dynamometers were mounted on reinforced concrete blocks insulated from the building structure by a layer of cork. Starting was by hand.

The Petter A.V.1 engine, which was at one time a production design until superseded by improved versions, has an 80 mm (3·15 inch) bore, 110 mm (4·33 inch) stroke, and a normal running speed of 1500 rev/min. Some modifications have been made to suit the engine for oil test work. The cast-iron cylinder head, which is detachable from the cylinder block, has single inlet and exhaust valves operated by push rods. The cylinder head also contains the air-cell combustion chamber, the top half of which is

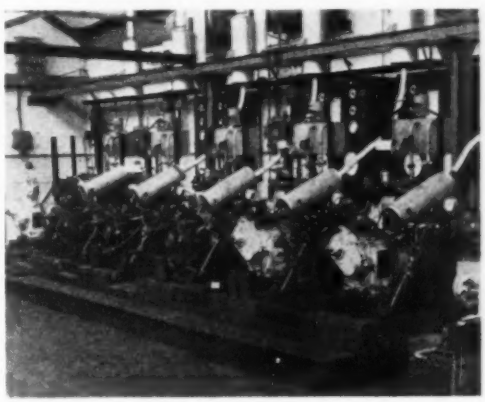


FIG 1
PETTER A.V.1 INSTALLATION

removable for inspection, and the injector, which is of the single-spray type. The unit has a piston and a wet liner which are easily removed and replaced. The piston is of aluminium alloy. The bearings throughout the engine are pressure-fed from an engine-driven plunger-type oil pump. The main bearings are one-piece thin-shell steel-backed bushes, white-metal lined. Large-end bearings are also of the thin-shell steel-backed type, lead-flash-coated copper–lead-lined top half and white-metal-lined lower half. The small-end bush is Admiralty gun-metal. Cylinder lubrication is provided by splash from the large-end bearings. An oil sampling valve is provided in the pressure oil system to enable samples to be taken. A metal gauze filter is fitted which is easily accessible for cleaning and inspection. The crankcase interior

* MS received 18 March 1957.

† Admiralty Oil Laboratory, Brentford.

is painted with oil-resistant paint to seal the casting and facilitate removal of deposits.

The engine coolant system, which employs kerosine as the working fluid, contains a water heat exchanger, and the temperature is controlled in the installations at A.O.L. by a magnetic valve in the raw water circuit operated by a thermoswitch of the bi-metal type. Although, in general, oil temperature is not controlled, a thin-walled steel cooling coil is fitted in the sump, through which raw water may be circulated to compensate for changes in ambient temperature.

During initial running, trouble was experienced with the fuel injector. The recorded exhaust temperature was erratic, and the exhaust smoke was at times excessive. This erratic injector performance was attributed to the periodic shut-down to assess engine oil consumption (every 12 hours). It is probable that at each shut-down a soak-back of heat was occurring which eventually caused injector needle sticking due to the formation of lacquer. To obviate this it was considered desirable that the test should run continuously. To enable oil consumption to be assessed, a sight glass was fitted to the sump, the top of which was vented to the crankcase interior to avoid pulsing. Subsequent operation has shown that an injector will now operate satisfactorily throughout the whole test.

Fuel input to the engine is controlled by an adjustable fuel stop which limits the movement of the fuel pump rack under the action of the engine governor. Actual fuel consumption of the engine is measured by means of special graduated bottles. To eliminate erratic running due to aeration of the fuel line, a capacity chamber is fitted on the A.O.L. engines immediately prior to the fuel pump.

TEST PROCEDURE

The procedure followed was that laid down for the AT/4 procedure [2] as modified slightly by the Engine Tests of Lubricants Panel of the Institute of Petroleum.

(1) *Assembly*

A new piston and set of rings were fitted for each test. These were manufactured specially for oil test purposes to special tolerances. Three compression rings, of which the lower two were taper turned, and a slotted scraper ring were fitted, while the upper scraper ring groove was left clear. The top and bottom faces of the top compression rings were lapped to give the required side clearance, the taper-turned rings were lapped on the lower face only. The top compression and scraper rings were then lapped on the periphery in a liner reserved for this purpose. The second and third compression rings were very lightly lapped on the periphery, sufficient to remove any burrs but not sufficient to move the taper.

A new liner was fitted after several tests when the maximum wear or ovality exceeded the specified limits.[2] New connecting rod bearings were fitted when the lead plating had worn through, and new main bearings were fitted when any signs of fatigue failure became evident.

Before assembly, the crankcase was flushed with white spirit. The piston and rings were cleaned in white spirit, measured, and weighed before fitting in the engine. The liner was fitted and measured in the block.

(2) *Run-in*

The engine was run-in for 8 hours on the schedule shown in Table I, using the test oil as a lubricant.

TABLE I

Running-in Conditions

Duration, hours	Load, b.h.p.	Jacket outlet temperature, °C	Speed, rev/min	Sump oil temperature, °C
2	1·5	50	1500	55 max
2	3·0	60	1500	55 max
3	4·0	75	1500	55 max
1	4·9	75–80	1500	55 max

Following the run-in, the oil was drained whilst still hot and the crankcase emptied by means of a syringe. The oil system was then re-charged with fresh test oil.

(3) *Test Operation*

Having refilled the engine with unused oil, the test was started. The engine was operated continuously under the conditions shown in Table II for 120 hours. At the end of each 24-hour period the crankcase oil level was checked and, if necessary, test oil weighed in to bring the oil up to the 5-pint level on the sight glass. All oil charged to or drained from the engine was weighed so that the oil consumption could be accurately determined.

TABLE II

IP Modified AT/4 Procedure Engine Test Conditions

Coolant	Kerosine
Engine speed, rev/min	1500
Load	Sufficient to produce a fuel consumption of 2·4 ± 0·05 lb/hour
Jacket outlet temperature, °F	185 ± 1
Jacket inlet temperature, °F	172 ± 2
Coolant flow, gal/hr	240 ± 10
Sump oil temperature, °F	131 to 167
Oil pressure, lb/sq. in.	10 ± 5
Duration of test, hours	120
Oil change	None

(4) *Assessment of Results*

After test, the engine was stripped and the appropriate parts washed, photographed, weighed, rated,

and measured. The terminology used to describe various engine conditions is given elsewhere,[3] together with details of the method used to rate the amount of carbon, lacquer, and sludge deposits on various parts of the engine. As explained,[3] this differs from the AT/4 method,[2] but the A.O.L. system enables one method to be used for all types of engine operated at A.O.L. and facilitates the comparison of the performance of oils in the Petter engine with their performance in the Caterpillar engine.

In the original AT/4 method [2] merits are awarded by first assessing demerits and then subtracting from the possible maximum value. This appears to involve unnecessary labour, besides confusing the issue to some extent, since this laboratory is concerned with the amount of deterioration products rather than the amount of clean areas. Also, in the original method, some ratings were weighted, and the sum of the weighted ratings was taken as the general index of the performance of an oil. In the A.O.L. method demerits are used directly and weighting is not attempted.

It may appear unfair that the original method of rating was not employed, but it has become apparent from contact with representatives of the oil industry that little reliance is placed on the general index. Further, separate consideration of each type of deposit seemed to be desirable, and accordingly this has been done.

OILS TESTED

The quality of the oils tested varied from that commonly known in industry as " Supplement 1 " to below the present DEF-2101-A (OMD 110) level. Oils A, B, and C of about Supplement 1 level were obtained specially by A.O.L. for a programme on the Caterpillar 1A oil test engine. They were used in the Petter engine programme because the Caterpillar data was available, and this made it possible to extend the quality range of the oils tested. Oil R, also of about Supplement 1 quality, was obtained from Naval Stores. Oils D, K, and P, which met DEF-2101-A Specification, were also drawn from Naval Stores. Oil G, also from Naval Stores, was of poor quality which had been shown not to meet DEF-2101-A requirements. Oil M from Naval Stores was an OMD 111 oil of low performance. Oils IPA, IPB, IPC, and IPD were supplied through the auspices of the IP Engine Tests of Lubricants Panel for a correlation programme of tests on Petter A.V.1 engines and provided a range of four oils of performance varying from U.S. Army 2-104B to Supplement 1 level.

Analytical data for these oils are given in Table III.

TABLE III

Analytical Data on Unused Oils

Oil	A	B	C	D	G	K	M	P	R	T	V	IPA	IPB	IPC	IPD
Specific gravity, 60° F/60° F	0·907	0·902	0·892	0·903	0·888	0·919	0·935	0·889	0·890	0·907	0·905	0·895	0·909	0·905	0·886
Flash point, P.M.C., ° F	370	430	405	410	335	405	380	405	405	425	425	450	400	390	425
Pour point, ° F	+5	−5	−5	−5	+20	+10	0	+5	−5	+5	−5	0	−5	+5	0
Sulphur, % wt	0·34	1·25	1·16	1·0	0·4	0·8	2·2	0·7	0·9	1·2	1·0	0·9	0·9	1·1	0·8
Copper corrosion	Slight discoloration	Pass	Pass	Pass	Pass	Pass	Brown	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Slight discoloration
Viscosity at 100° F, cS	119	113	130	112	114	136	126	114	112	112	109	111	112	107	121
Viscosity at 210° F, cS	11	11	13	10	12	11	11	12	12	10	10	11	10	10	12
Viscosity index	72	94	96	71	100	69	70	100	96	74	71	89	69	78	100
Initial pH (ASTM.D664/51)	10·0	10·1	11·8	9·0	8·4	8·0	8·5	7·5	9·7	8·3	7·4	8·8	8·3	9·9	105
Total base number (pH 4)	4·0	4·2	3·1	2·0	1·3	2·0	0·9	1·4	4·9	2·3	1·9	1·0	0·8	1·3	5·1
Carbon residue, % wt	1·1	1·2	1·4	0·9	0·6	0·7	0·8	0·7	1·0	0·8	0·9	0·5	0·8	1·0	0·9
Sulphated ash, % wt	1·04	1·24	1·22	0·77	0·32	0·57	0·55	0·33	0·82	0·80	0·77	0·33	0·64	0·76	0·79
Water, % vol	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil

FUEL USED

The high-sulphur tests were all performed on a single supply of 0·9% wt sulphur-content gas oil earmarked as a reference fuel for the use of A.O.L. and meeting the fuel requirements of Admiralty specifications. The low-sulphur tests were performed on various practically-identical supplies of IP gas oil, with a sulphur content of about 0·4% wt, meeting the fuel requirements of the MIL-L-2104A and the DEF-2101-A specifications.

Analytical data for these fuels are given in Table IV.

TABLE IV

Analytical Data on Fuels

	0·9% wt sulphur	0·4% wt sulphur
Appearance	Clear	Clear
Specific gravity, 60° F/60° F	0·839	0·859
Flash point, ° F	186	186
Pour point, ° F	+15	−15
Cloud point, ° F	26	0
Viscosity at 100° F, cS	3·5	3·7
Initial boiling point, ° C	200	204
Final boiling point, ° C	365	364
Total distillate, % vol	98·0	98·5
Organic acidity, mg KOH/gm	0·013	1·00
Inorganic acidity, mg KOH/gm	Nil	Nil
Sulphur, % wt	0·88	0·43
Carbon residue, % wt	0·18	0·16
Water, % vol	Nil	<0·01
Ash, % wt	<0·01	<0·01
Calorific value (gross), B.t.u./lb	19,620	19,530
Cetane number	59	43
Sediment by extraction, % wt	<0·01	<0·01

REPEATABILITY OF RESULTS *

The first six oils tested in the Petter A.V.1 engine at A.O.L. were tested twice, once on each of two engine installations, so as to provide data relating to the repeatability of the test results. Four oils were the IP Correlation Oils, while the other two oils had been tested extensively at A.O.L. in other engines. The former were tested with 0·4% wt sulphur fuel and the latter with 0·9% wt sulphur fuel.

The results have been analysed statistically on the assumption of an orthogonal pattern. The comments which follow as to the significance of the results are derived from the results of this analysis.

(1) *Top Ring Groove Carbon*

Following on from the custom with the Caterpillar test engine, the amount of carbon in the top ring groove was assessed. The results from the first six oils are shown in Table V, together with the test numbers. The same order is used in the subsequent Tables VI–XI.

TABLE V

Results—Top Ring Groove Carbon

Oil	Approximate quality level	First engine		Second engine	
		Test No.	Result	Test No.	Result
R	Supplement 1	EP/1	0	EP/2	6·3
D	DEF-2101-A	EP/3	3·0	EP/4	3·0
IPA	U.S. Army 2-104B	EP/5	5·0	EP/6	8·0
IPB	Fail DEF-2101-A	EP/7	5·0	EP/8	7·0
IPC	DEF-2101-A	EP/9	5·0	EP/10	2·0
IPD	Supplement 1	EP/11	4·0	EP/12	3·0

There was no significant difference between the results given by different oils.

(2) *Total Ring Groove Carbon*

Since the oil had no significant effect on the amount of carbon in the top ring groove, the average carbon in all the ring grooves was assessed. In the Petter engine all the rings normally fill with carbon to some extent, whereas in the Caterpillar engine usually only the top ring groove receives carbon, and it was considered that the total ring groove carbon might be a more significant criterion. The results from the first six oils are shown in Table VI.

TABLE VI

Results—Total Ring Groove Carbon

Oil	Approximate quality level	First engine	Second engine
R	Supplement 1	0·1	2·1
D	DEF-2101-A	1·5	1·5
IPA	U.S. Army 2-104B	2·1	4·2
IPD	Fail DEF-2101-A	2·0	3·2
IPC	DEF-2101-A	3·2	1·5
IPD	Supplement 1	1·6	1·3

Again, there was no significant difference between the results given by the different oils.

(3) *Ring Sticking*

Ring sticking is not very often encountered on the Petter test with oils of DEF-2101-A and Supplement 1 quality, so it was noteworthy that on both tests with oil " IPA " a ring stuck, whereas no stuck rings were encountered with any of the tests on the other five oils. On Test No. EP/5 the top ring stuck for 15°, and on Test No. EP/6 the second ring stuck for 15°.

(4) *Crown Land Cutting*

The crown land cutting results from the first six oils are given in Table VII.

TABLE VII

Results—Crown Land Cutting

Oil	Approximate quality level	First engine	Second engine
R	Supplement 1	1·3	1·1
D	DEF-2101-A	2·0	3·4
IPA	U.S. Army 2-104B	2·8	3·8
IPB	Fail DEF-2101-A	4·0	3·6
IPC	DEF-2101-A	3·8	1·6
IPD	Supplement 1	4·8	5·8

It appeared that the oil had a significant effect on the amount of crown land cutting.

(5) *Land Lacquer*

The land lacquer (*i.e.* the total lacquer on all the piston-ring lands) results from the first six oils are given in Table VIII.

TABLE VIII

Results—Land Lacquer

Oil	Approximate quality level	First engine	Second engine
R	Supplement 1	0·8	2·0
D	DEF-2101-A	6·3	7·0
IPA	U.S. Army 2-104B	6·8	8·0
IPB	Fail DEF-2101-A	5·7	7·1
IPC	DEF-2101-A	4·7	9·5
IPD	Supplement 1	4·0	5·5

It appeared that both the oil and the engine affected the amount of land lacquer, the second engine consistently giving more lacquer than the first engine. This was the only instance in which an engine effect appeared and the reason for it is not clear.

* " Repeatability " to be applicable as normally understood should involve one operator, one engine, and one laboratory. In the tests herein described it has been necessary to use two engines and a team of operators. However, this is not considered to give the results the status of " reproducibility," *i.e.* different operators, different engines, and different laboratory.

TABLE IX
Results—Ring Groove Lacquer

Oil	Approximate quality level	First engine					Second engine				
		Top	2nd	3rd	Scraper	Total	Top	2nd	3rd	Scraper	Total
R	Supplement 1	1·0	1·0	0·6	0	0·7	6·5	2·5	2·2	0	2·8
D	DEF-2101-A	7·8	8·8	6·0	0·8	5·9	7·0	6·3	3·3	0	4·2
IPA	U.S. Army 2-104B	8·1	10·0	9·4	3·8	7·8	10·0	10·0	10·0	4·3	8·6
IPB	Fail DEF-2101-A	6·7	3·9	9·5	6·5	6·7	8·2	10·0	10·0	5·5	8·4
IPC	DEF-2101-A	6·0	8·0	9·0	5·8	7·2	5·5	10·0	10·0	9·6	8·8
IPD	Supplement 1	5·0	3·0	2·5	0	2·6	5·6	4·2	4·0	1·2	3·8

(6) *Ring Groove Lacquer*

The ring groove lacquer results from the first six oils are given ring by ring in Table IX.

In no case was the engine effect significant. The significance of the oil effect varied from groove to groove, the deposits in the top groove not being significant, in the second groove the effect was significant, in the third groove the effect was highly significant, and in the scraper groove it was very significant. The total effect was very significant, the non-significant top groove having reduced the significance of the total.

(7) *Skirt Lacquer*

The skirt lacquer results from the first six oils are given in Table X.

TABLE X
Results—Skirt Lacquer

Oil	Approximate quality level	First engine	Second engine
R	Supplement 1	0	0
D	DEF-2101-A	0·5	0·5
IPA	U.S. Army 2-104B	0·7	1·3
IPB	Fail DEF-2101-A	0·8	0·6
IPC	DEF-2101-A	0·6	0·9
IPD	Supplement 1	0	0·1

It appeared that the oil effect was significant, but that the engine effect was not.

(8) *General Sludge*

The amount of general sludge obtained with the six oils is given in Table XI.

TABLE XI
Results—General Sludge

Oil	Approximate quality level	First engine	Second engine
R	Supplement 1	1·7	1·7
D	DEF-2101-A	2·2	2·7
IPA	U.S. Army 2-104B	5·8	5·8
IPB	Fail DEF-2101-A	3·3	3·3
IPC	DEF-2101-A	1·1	1·1
IPD	Supplement 1	1·7	1·7

It appeared that the oil effect was highly significant. It should be remembered, however, that sludge is difficult to rate, and since the tests were performed in pairs, there may have been some bias towards assessing the deposits equally.

(9) *Wear*

It was A.O.L. experience that the most reliable criterion of wear was given by measurements of ring weight loss, usually quoted as total ring weight loss, *i.e.* including all the rings. The ring weight losses obtained with the six oils are given in Table XII.

TABLE XII
Results—Ring Weight Loss

Oil	Approximate quality level	First engine	Second engine
R	Supplement 1	140	84
D	DEF-2101-A	94	65
IPA	U.S. Army 2-104B	114	138
IPB	Fail DEF-2101-A	114	66
IPC	DEF-2101-A	103	75
IPD	Supplement 1	85	82

It appeared that the oil had no effect on the wear rate.

PETTER–CATERPILLAR CORRELATION

The main reason for the installation of the Petter A.V.1 engines at A.O.L., as at many other laboratories, was to provide means whereby an indication of the Caterpillar assessment of the performance of an oil could be obtained more rapidly and cheaply. In other words, it had been considered that it was possible to predict what the performance of an oil in the Caterpillar engine would be from a consideration of its performance in the Petter engine.

In the course of experiments at A.O.L., many oils have been tested in both a Petter A.V.1 engine, using the AT/4 procedure, and a Caterpillar engine, using either 0·4 per cent sulphur or 0·9 per cent sulphur fuel. Comparable results from such pairs of tests are shown in Table XIII, and graphical correlations are shown in Figs 2–8.

TABLE XIII

Petter A.V.1 and Caterpillar Results

	Oil	Test No.	Top ring groove carbon	Crown land cutting	Land lacquer	Ring groove lacquer-carbon	Skirt lacquer	General sludge	Total ring weight loss, mg
					Petter A.V.1 engine				
0·4% wt sulphur fuel	D	EP/33	5·0	2·0	5·2	5·3 (5·0)	0·5	2·5	152
	G	EP/17	5·0	4·8	5·4	6·2 (4·6)	0·4	1·7	202
	P	EP/35	3·5	1·8	5·7	7·3 (3·3)	0·9	2·5	178
	U	EP/43, EP/47	5·0	2·5	6·7	5·7 (4·2)	0·5	2·2	101
	V	EP/42	3·5	1·5	6·3	4·8 (4·0)	0·7	2·5	160
	Y	EP/44	6·0	1·0	7·7	7·1 (5·9)	0·2	2·5	133
	AA	EP/46	5·0	1·0	6·8	6·3 (5·3)	0·1	2·0	86
	IPA	EP/5, EP/6	6·5	3·3	7·4	8·2 (5·3)	1·0	5·8	126
	IPB	EP/7, EP/8	6·0	3·8	6·4	7·5 (3·3)	0·7	3·3	90
	IPC	EP/9, EP/10	3·5	2·7	7·1	8·0 (2·4)	0·7	1·1	89
	IPD	EP/11, EP/12	3·5	5·3	4·7	3·2 (2·3)	0·1	1·7	83
0·9% wt sulphur fuel	A	EP/31	2·0	3·3	5·9	4·0 (1·3)	0·3	1·3	110
	B	EP/14	1·0	1·3	6·9	6·3 (1·9)	1·2	3·3	105
	C	EP/28	3·0	2·5	4·5	4·9 (2·4)	0·6	1·7	102
	D	EP/3, EP/4	3·0	2·7	6·6	5·0 (4·1)	0·5	2·4	80
	G	EP/36	7·0	2·5	8·6	7·8 (6·0)	1·3	2·5	366
	K	EP/22	2·0	5·0	4·5	4·8 (4·2)	0·6	1·7	212
	M	EP/27	4·0	3·8	7·4	7·2 (3·5)	0·5	3·3	170
	P	EP/24	6·0	3·3	6·9	9·1 (5·0)	0·9	2·5	155
	R	EP/1, EP/2	3·8	2·1	2·0	2·1 (1·8)	0	1·8	109
	T	EP/13, EP/38 EP/39	2·5	1·3	8·3	5·3 (1·6)	1·4	2·9	168
					Caterpillar engine				
0·4% wt sulphur fuel	D	EC/6	2·4	0·5	0	1·9 (1·9)	0	1·0	493
	G	EC/24	2·8	2·0	0·6	2·9 (2·4)	0	1·5	992
	P	EC/29	3·1	2·0	0	1·1 (1·0)	0	2·5	479
	U	EC/45	0·1	1·6	6·2	7·0 (1·3)	0	1·5	523
	V	EC 39	2·9	1·5	3·4	4·7 (0·9)	trace	2·5	450
	Y	EC/44	3·3	1·2	0·4	1·8 (1·5)	0	1·5	301
	AA	EC/42	0·4	2·0	trace	1·7 (1·1)	trace	2·0	1585
	IPA	IP	2·9	N.A.	9·0 *	N.A.	trace	N.A.	N.A.
	IPB	IP	1·0	N.A.	0·4 *	N.A.	0	N.A.	N.A.
	IPC	IP	0·1	N.A.	0·1 *	N.A.	0	N.A.	N.A.
	IPD	IP	0·1	N.A.	0·1 *	N.A.	0	N.A.	N.A.
0·9% wt sulphur fuel	A	EC/12	2·5	2·5	0	2·2 (2·0)	0	0·5	1054
	B	EC/14, EC/18	1·7	2·2	0	1·2 (0·7)	0	0·5	713
	C	EC/16	2·0	2·5	0	1·0 (1·0)	0	1·0	1473
	D	EC/13	4·4	2·0	0·3	3·1 (2·3)	0	1·0	820
	G	EC/23, EC/25	6·5	2·2	9·6	9·1 (3·1)	trace	2·0	2817
	K	EC/26	3·5	2·5	3·3	5·2 (3·0)	0	0·5	1573
	M	EC/28	4·7	2·8	8·4	6·8 (2·5)	0	1·0	1777
	P	EC/27	4·3	3·0	3·6	4·7 (2·3)	0	1·0	2351
	R	EC/9, EC/10, EC/17	2·7	2·0	0	1·3 (0·8)	0	1·1	831
	T	EC/38	4·8	1·8	3·3	4·7 (1·9)	0	2·5	761

N.A. = Not available. * Estimated by A.O.L.

(1) *Top Ring Groove Carbon*

The Petter top ring groove carbon is plotted against Caterpillar top ring groove carbon in Fig 2. It can be seen that there is no correlation.

(2) *Crown Land Cutting*

The Petter crown land cutting is shown plotted against the Caterpillar crown land cutting in Fig 3. There appears to be an approximate relationship, although more results are required to confirm this. However, there is certainly nothing to justify prediction of Caterpillar results from the Petter results.

(3) *Land Lacquer*

The land lacquer for the Petter and Caterpillar engines is shown in Fig 4. Again it appears as if there might be an approximate relationship, although more results are required to prove this. But again there is certainly nothing to justify prediction of Caterpillar results from the Petter results.

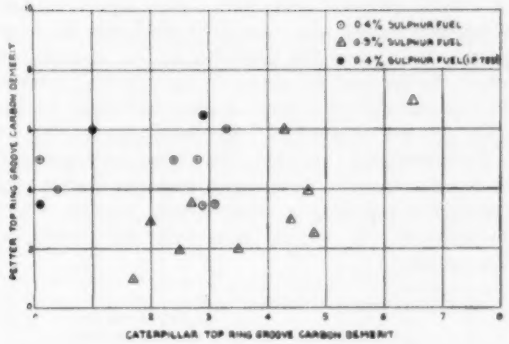


FIG 2

CORRELATION BETWEEN PETTER TOP RING GROOVE CARBON AND CATERPILLAR TOP RING GROOVE CARBON

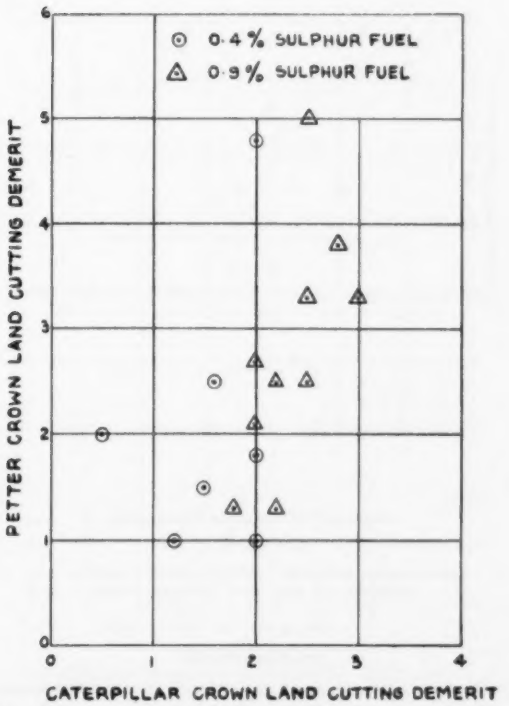


FIG 3

CORRELATION BETWEEN PETTER CROWN LAND CUTTING AND CATERPILLAR CROWN LAND CUTTING

(4) *Ring Groove Lacquer*

The ring groove lacquer for the Petter and Caterpillar engines is shown in Fig 5. There is little evidence of any relationship, and again there is certainly nothing to justify prediction of Caterpillar results from the Petter results.

(5) *Skirt Lacquer*

Since lacquer so rarely occurs on the skirt of the Caterpillar piston, it is hardly practical to plot the results in comparison with those obtained from the Petter engine. However, it is noteworthy that only

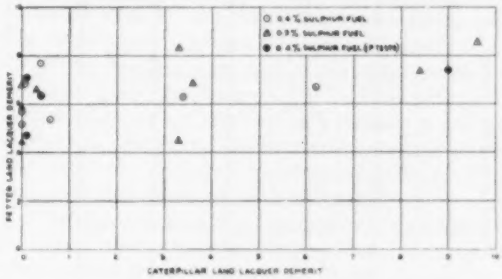


FIG 4

CORRELATION BETWEEN PETTER LAND LACQUER AND CATERPILLAR LAND LACQUER

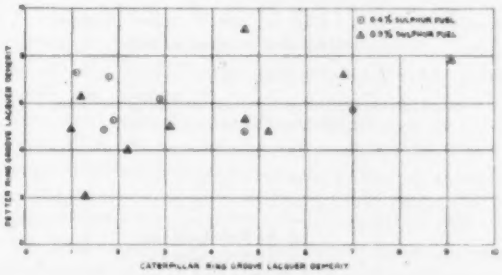


FIG 5

CORRELATION BETWEEN PETTER RING GROOVE LACQUER AND CATERPILLAR RING GROOVE LACQUER

two of the four oils of inferior performance, which in the Caterpillar gave a trace of lacquer on the skirt, gave high skirt lacquer in the Petter engine, which fact suggests that the degree in correlation would not be great.

(6) *General Sludge*

The general sludge from the Petter engine is compared with the general sludge from the Caterpillar engine in Fig 6. It can be seen that the Caterpillar performance could not be predicted from the Petter result.

(7) *Wear*

The total piston ring wear from the Petter and Caterpillar engines is shown in Fig 7. It can be seen that there is no correlation.

(8) *Petter Lacquer–Caterpillar Carbon*

Probably the most critical indicator of the performance of an oil in the Caterpillar is the amount of carbon in the top ring groove, whilst the critical indicator for the Petter is the amount of lacquer on

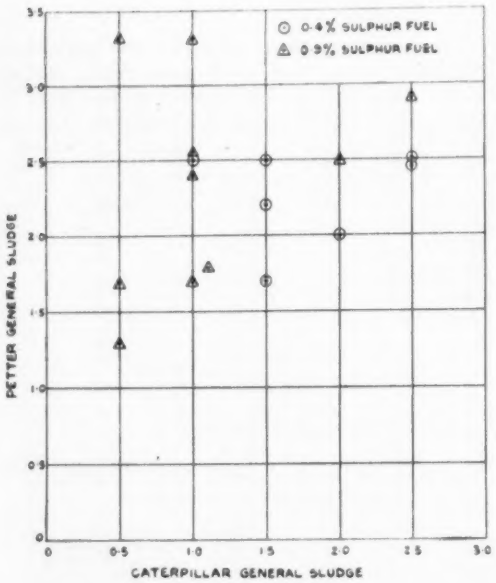


FIG 6

CORRELATION BETWEEN PETTER GENERAL SLUDGE AND CATERPILLAR GENERAL SLUDGE

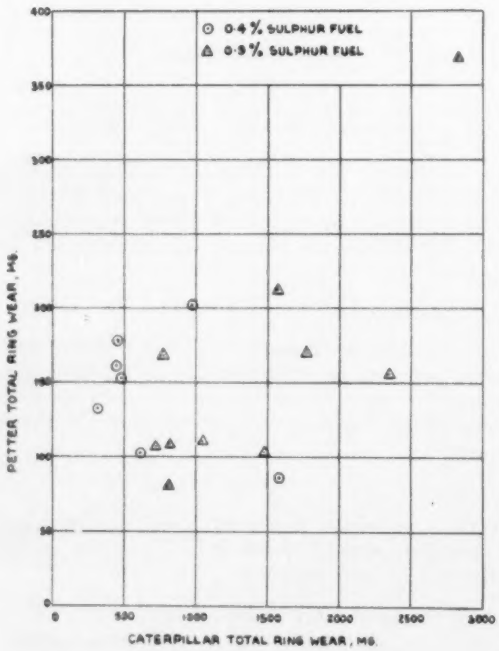


FIG 7

CORRELATION BETWEEN PETTER TOTAL RING WEAR AND CATERPILLAR TOTAL RING WEAR

the land, grooves, and skirt. Although it is not altogether logical, some operators claim that they can predict the Caterpillar performance, *i.e.* meaning in effect the amount of carbon in the top ring groove, from a consideration of the amount of lacquer on the land, grooves, and skirt of the Petter piston.

To investigate this claim, the Petter land, grooves, and skirt lacquer have been plotted against the Caterpillar top ring groove carbon in Figs 8—10 respectively. It can be seen that the results do not correlate.

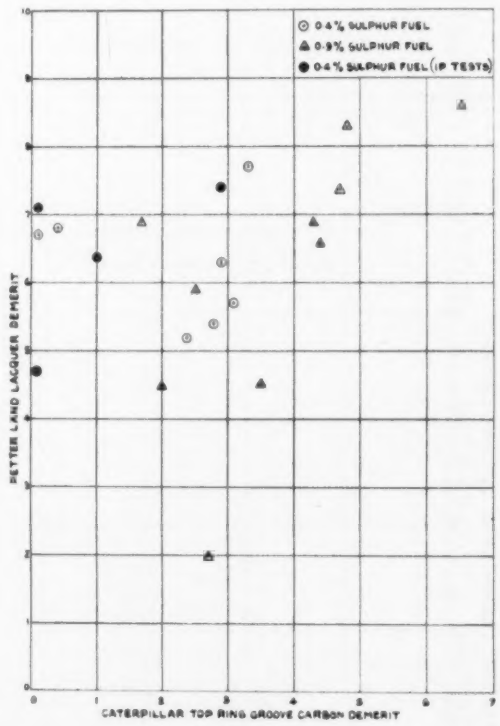

⊙ 0·4% SULPHUR FUEL
△ 0·9% SULPHUR FUEL
● 0·4% SULPHUR FUEL (IP TESTS)
PETTER LAND LACQUER DEMERIT
CATERPILLAR TOP RING GROOVE CARBON DEMERIT

FIG 8

CORRELATION BETWEEN PETTER LAND LACQUER AND CATERPILLAR TOP RING GROOVE CARBON

DISCUSSION

It has been shown that there was a significant difference on the Petter A.V.1 engine using the IP modified AT14 procedure between the performance of oils as regards the crown land cutting, land lacquer, ring groove lacquer, skirt lacquer, and sludge, but not as regards ring groove carbon and wear. Despite this, however, these results could not be used to predict the performance of oils on the Caterpillar engine.

There may be several reasons for this lack of correlation, and one should be mentioned here. Oils tested in the Petter engine never assumed a Strong

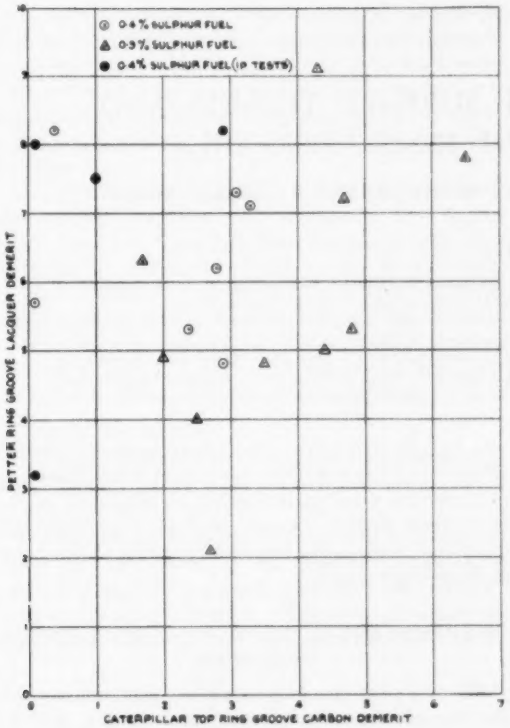

0·4% SULPHUR FUEL
0·3% SULPHUR FUEL
0·4% SULPHUR FUEL (IP TESTS)
PETTER RING GROOVE LACQUER DEMERIT
CATERPILLAR TOP RING GROOVE CARBON DEMERIT

FIG 9

CORRELATION BETWEEN PETTER RING GROOVE LACQUER AND CATERPILLAR TOP RING GROOVE CARBON

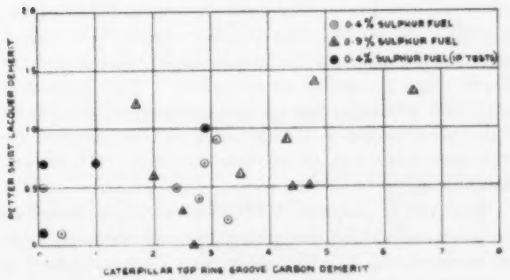

0·4% SULPHUR FUEL
0·3% SULPHUR FUEL
0·4% SULPHUR FUEL (IP TESTS)
PETTER SKIRT LACQUER DEMERIT
CATERPILLAR TOP RING GROOVE CARBON DEMERIT

FIG 10

CORRELATION BETWEEN PETTER SKIRT LACQUER AND CATERPILLAR TOP RING GROOVE CARBON

Acid Number. Thus, 120 hours operation of an oil in the Petter engine does not cause as much acidic deterioration in the oil as 120 hours operation in the Caterpillar engine. Presumably one factor responsible for this difference is that at A.O.L. the Petter oil consumption was higher than that of the Caterpillar engine, and consequently the additive was replenished to a greater extent. It may be possible that if the oil consumption and the amount of oil in the sump of the Petter engine was reduced, the results obtained would be more similar to those obtained in the Caterpillar engine.

It is perhaps relevant to recall here that A.O.L. is concerned with a wide variety of base stocks and types of additives. It may be possible for a particular laboratory handling only one or two base stocks or additives to use the Petter A.V.1 for Caterpillar prediction, since that laboratory may develop a certain correlation. However, another laboratory may develop another correlation relationship with another type of base stock or additive and would not be able to predict the results of the first laboratory's additives correctly. At A.O.L. the range of base stocks and additives is evidently too great for satisfactory results.

CONCLUSIONS

(1) There was a significant difference on the Petter A.V.1 engine using the IP modified AT/4 procedure between the performance of oils as regards the crown land cutting, land lacquer, ring groove lacquer, skirt lacquer, and sludge.

(2) There was no significant difference on the Petter A.V.1 engine using the IP modified AT/4 procedure between the performance of oils as regards top ring groove carbon, total ring groove carbon, and wear.

(3) The engine had no significant effect on the performance of oil in the Petter A.V.1 except for land lacquer.

(4) In none of the several ways examined could results of tests of oils on the Petter engine be used to predict the performance of the oils on the Caterpillar engine, even when considering factors shown to give significant differences on the Petter engine.

ACKNOWLEDGMENTS

Thanks are due to the Admiralty for permission to publish this paper. Thanks are also due to the Chief Scientist of the Admiralty Oil Laboratory, E. J. Widdowson, for his unfailing encouragement and assistance, to E. Dawson, who was responsible for the physical and chemical inspection of all the oil and fuel samples referred to in this paper, and to H. R. O. Jones, who was responsible for the day-to-day operation of the engines.

References

[1] Cree, J. C. *J. Inst. Petrol.*, 1953, **39**, 571.
[2] Towle, A., and Vaile, P. E. B. *J. Inst. Petrol.*, 1953, **39**, 581.
[3] Tourret, R., and Bale, R. W. *J. Inst. Petrol.*, 1956, **42**, 292.

THE MEASUREMENT OF THE SURFACE TENSION AND INTERFACIAL TENSION OF INSULATING OILS *

By L. MASSEY †, N. N. MURTY †, and C. N. THOMPSON ‡ (Associate Fellow)

SUMMARY

An investigation carried out on behalf of the Electrical Research Association concerning the measurement of interfacial tension of insulating oils shows that the existing IP method 90/55T needs modification.

In particular, since the interfacial tension values obtained are strongly dependent on the " age " of the interface, the time at which the measurement should be made needs to be specified, and a " one-minute " value is recommended for all future work. Other modifications of apparatus and procedure have also proved by experience to be of value in ensuring better precision, and a rigorous cleaning technique is regarded as essential. Some of the suggested improvements also apply to the method of measuring surface tension.

INTRODUCTION

THE interfacial tension of a hydrocarbon oil against water is largely a function of the type and concentration of polar molecules present. Such molecules, which may be present in an insulating oil as a result of oxidation or contamination, cause a lowering of the interfacial tension by migrating to and being adsorbed at the interface. Fatty acids and soaps are amongst those compounds whose presence effects the greatest reduction in the interfacial tension.

The deterioration of transformer oil in service is a matter for concern, since the presence of oil oxidation products and adventitious impurities greatly impairs the efficient functioning of the transformer and can lead to ultimate breakdown.

Among the laboratory tests which have been used or proposed for assessing the extent of deterioration of insulating oils, *e.g.* acid value, saponification value, interfacial tension, and power factor, it is considered by some [1] that interfacial tension is the most convenient and significant single test providing a number which can serve as an index or criterion of oil deterioration. Although this opinion of the universal applicability of the test is disputed by a strong body of opinion, it may at least be considered a useful adjunct to other tests, and may prove to have particular merit in following the earlier stages of deterioration of insulating oils.

In order to check its usefulness, and to correlate its results with those of other tests, the interfacial tension measurement was one of those chosen by Panel E/Ac of the Electrical Research Association (ERA) for the examination of samples from service of insulating oils used in field trials involving both inhibited and uninhibited oils. In the early stages of this programme the collaborating laboratories experienced some difficulty in obtaining satisfactory results, and at the request of the ERA an investigation was undertaken in the laboratories of " Shell " Research Ltd and Metropolitan-Vickers Electrical Co. Ltd into the glass plate method as described in the IP Method 90/55T. As an outcome, a modified and improved version was evolved, and this is described in the present paper.

EXPERIMENTAL FACTORS INFLUENCING PRECISION

The two most important standard methods suitable for the measurement of interfacial tension (I.F.T.) are those prescribed by the IP and the ASTM.

The IP method [2] first proposed in 1944 (IP 90/44P Method B) involves the measurement of the pull exerted on a vertically suspended rectangular glass plate with its lower edge in the interface between two liquids. Assuming zero contact angle, the pull is equal to the product of the interfacial tension and the lower edge perimeter of the plate. The method is intended primarily for an oil–water interface. With this specification is associated a related method for the measurement of surface tension (IP 90/44P Method A).

The ASTM method (D971–50), which is described as a procedure for measuring the interfacial tension of mineral oils against water, was first published in tentative form in 1948 and then adopted as standard in 1950. It involves the measurement of the force necessary to detach a horizontal planar ring of platinum upwards from the surface of the water at an oil–water interface.[3]

The two methods are commonly referred to as the glass plate and platinum ring methods respectively, and both depend on the use of a torsion balance of the Du Noüy type. There are accepted advantages and disadvantages for both methods and, as a result, differing opinions exist regarding relative overall merits.

* MS received 1 May 1957. † Metropolitan-Vickers Electrical Co. Ltd. ‡ " Shell " Research Ltd.

A third method of measurement of interfacial tension is available in the more elaborate pendent drop technique.[4] This is considered to be much more accurate than either of the other methods, but it is unsuitable as a standard test method, being time-consuming and demanding specialized apparatus and facilities.

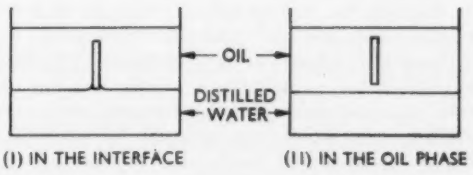
Of these three methods ERA Panel E/Ac considered that the IP glass plate method was the most appropriate for their purposes and suggested that this investigation should be aimed at the improvement of the techniques and precision of this tentative method. The current edition (IP 90/55T) is based on the one proposed in 1944. The considerations on which are based the modified form of the test given in the final section of this paper are as follows:

(1) *Age of the Interface*

A clause specifying the " age " of the interface at which the interfacial tension is to be reported should be included in the method.

This is necessary because of the substantial changes which can be caused by the gradual migration of polar (hydrophilic) materials from the bulk of the oil to the oil–water interface. The rate of migration depends on the type and concentration of the polar

FRONT ELEVATION OF GLASS PLATE



LOCATION OF THE PLATE AT MEASUREMENT

FIG 1

VIEW AND LOCATION OF THE GLASS PLATE AT MEASUREMENT OF INTERFACIAL TENSION

molecules which are present in oxidized and deteriorated transformer oils, on the nature of the oil medium, and on other factors such as temperature. The behaviour of typical insulating oils is illustrated in Fig 2. These results were obtained using an early version of the " Shell " glass plate method based on the original form developed in 1948. The results would not necessarily correspond with those obtained by the method now recommended, but they are sound comparative values. It is clear that the time dependence is different for different oils and is not a function of the level of the I.F.T. values of the oil in

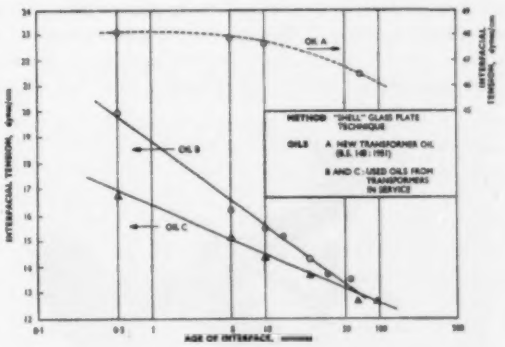

OIL A
OIL B
OIL C
METHOD "SHELL" GLASS PLATE TECHNIQUE
OILS A NEW TRANSFORMER OIL
B AND C : USED OILS FROM TRANSFORMERS IN SERVICE
AGE OF INTERFACE, minutes

FIG 2

VARIATION OF INTERFACIAL TENSION VALUES WITH AGE OF INTERFACE

question. Furthermore, whilst the values when plotted against the logarithm of time often give straight lines (oils B and C), this is not always the case (oil A). The usual trend is for values to decrease with time, and several hours may be necessary for an equilibrium or steady-state value to be attained. This may be considerably lower than values measured in the first few minutes.

The age of the interface at which a " true " I.F.T. is given is a matter of opinion. It may be argued that the true value is at zero time because this represents the condition of the original oil sample before its properties are modified by the interchange of polar molecules with water which necessarily occurs under the test conditions. On the other hand, it may be held that the equilibrium value at infinite time is the nearest approach to the true value. Neither of these " true " values is experimentally convenient. The value at zero time is likely to be subject to large errors if attempts are made to determine it directly, and extrapolation methods are not considered to be desirable. The preparation of a curve to calculate the value at infinite time is tedious. For practical purposes it will probably be generally agreed that the value recorded after one minute from the formation of the interface is an acceptable index of the presence of hydrophilic constituents in oil. The I.F.T. value after this time also has the merit that it is already quoted in the ASTM platinum wire method, and its adoption will facilitate correlation between the results of the two national methods. For these reasons the " one-minute " value is now recommended. This value can, with experience, be directly determined,

but if difficulty is encountered it can be obtained by extrapolation.

(2) *Form of the Glass Plate*

The IP plate measuring 30–40 mm × about 5 mm and provided with a straight glass stem has three disadvantages: a plate of the maximum length of 40 mm is too large for use in a glass dish of the specified diameter of 50 mm, for with these measurements "end" errors may be encountered; the adjustment of the lower edge parallel with the water surface is difficult; and the plate is very fragile. An improved form of plate is obtained by changing the dimensions to 20 mm × 10 mm × 0·1 mm and by providing a zig-zag in the glass stem. Being more compact in shape, this plate is more robust, and, moreover, it is free from end errors when used in the specified dish. The advantage provided by the inclusion of a zig-zag stem is that adjustment of the plate in a position parallel to the liquid surface is greatly facilitated by heating one or more of the bends of the zig-zag rod in a flame.

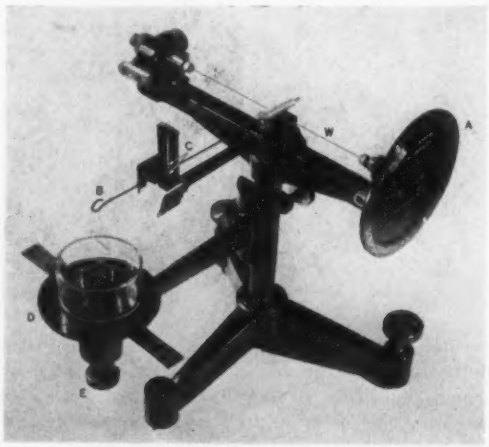


FIG 3
DU NOÜY TENSIOMETER

(3) *Cleaning Procedure*

The plate cleaning procedure of IP 90/55T involving successive washes in chromic acid, tap water, and distilled water has been found to be insufficiently rigorous. This washing procedure was followed by a slight etch in dilute hydrofluoric acid to ensure that the plate would be wetted by water after immersion in oil. This etched surface has been found to favour contamination.

It has been proved experimentally that a washing sequence of benzene, acetone, distilled water, chromic acid, and redistilled water produces a satisfactory plate, and when this sequence has been correctly observed there is no need to etch the plate with hydrofluoric acid. Tap water must not be used at any stage, despite the fact that its use was permitted in earlier methods, and the redistilled water used after the chromic acid treatment must be twice distilled, the second time from potassium permanganate.

(4) *Calibration of Equipment*

The accurate determination of I.F.T. is an operation calling for a high degree of cleanliness in the equipment and of care in the preparation of the distilled water. These matters are difficult to ensure, and even the most careful worker requires some positive evidence that his equipment, materials, and general technique are correct before proceeding with the determination of I.F.T. on the sample. A simple check is fortunately possible. Distilled water has a surface tension of 72·8 dynes/cm at 20° C, and if the surface tension of the water in the test dish is determined immediately before the oil sample is added, then a result of between 71 and 73 dynes/cm is evidence that the equipment is sufficiently clean and that the distilled water is satisfactory. If the water fails to reach this value, then a step-by-step examination of water and equipment must be made to establish the cause of the incorrect value.

(5) *Plate Manipulation*

The end-point in the measurement of the pull on the glass plate may be taken either by breaking the lower edge of the plate off the interface by simultaneous manipulation of the table and the torsion head, or by bringing the torsion arm back to zero by manipulating the torsion head only, the lower edge never being broken off the interface. The former gives greater precision, but permits adsorption of oil components on the lower edge of the glass plate. This may lead to erratic results if repeated measurements are required for extrapolation purposes, and it is therefore necessary to clean the plate after each measurement, which is very tedious. The latter technique is less precise, but it avoids contamination of the glass and permits repeated measurements after increasing time intervals to be made. It is therefore to be preferred.

There are also two possible starting arrangements for the glass plate. In the procedure given in IP 90/55 the plate is first balanced while suspended wholly in the oil, after which its lower edge is introduced into the interface. This permits oil contamination of the glass and makes it difficult to time the operations so that the first measurement of interfacial tension is made at the desired "age" of the interface. The alternative procedure is to start with the plate balanced with its lower edge in water and then to add carefully the oil. This avoids possible contamination of the edge of the plate. It also permits the age of

the interface to be measured accurately and is the preferred method.

By combining these two methods of plate manipulation with the calibration operation using distilled water, a simple, convenient, and efficient method results, *i.e.* the surface tension of the water is determined to check equipment and materials, then, without removing the edge of the plate from the water surface, oil is added, and finally, without breaking the edge of the plate from the interface, a number of readings can be taken after the desired time intervals with no fear of contamination.

(6) *Precision*

In the present work the number of results obtained using the final version of the method based on the modifications given in (1) and (5) is insufficient to allow an accurate statistical estimate of precision to be made. The experience gained suggests that the method should yield results which are repeatable to 2 dynes/cm and reproducible to 4 dynes/cm. These figures may be on the optimistic side, since the work has been done largely on either new oils, or oils not in an advanced state of deterioration. With more highly oxidized products the precision may be worse, but this is of lesser practical importance because the chief value of the test lies in its ability to discriminate between oils in their early stages of deterioration.

(7) *Correlation with Other Methods*

The results obtained using the final version of the glass plate method are generally about 1–2 dynes/cm lower than the corresponding values obtained for the same oils using platinum wire ASTM method, and about 3 dynes/cm lower than the figures obtained by the pendent drop technique.

Procedures for the measurement of surface tension and of interfacial tension which include the above suggestions are given below, the method format being that suggested in the introduction of the IP Handbook.[2]

GLASS PLATE METHODS FOR THE DETERMINATION OF SURFACE AND INTERFACIAL TENSION

SCOPE

(1) These two methods are for the measurement of surface tension and interfacial tension of liquids having a normal boiling point of 50° C or higher. Method A measures the surface tension of liquids. Method B is intended for the measurement of interfacial tension between water and oil, the oil being of lower density, but it is applicable to other liquid pairs provided that the lower layer wets the plate preferentially.

OUTLINE OF METHODS

(2) The pull on a vertical thin glass plate with its lower edge in the surface of a liquid or in the interface of two liquids is measured by means of a torsion balance. Assuming zero contact angle, the pull is equal to the product of the surface or interfacial tension and the lower edge perimeter of the plate.

APPARATUS

(3) (*a*) *Torsion Balance* (Fig 3)—of the conventional du Noüy type, consisting essentially of a horizontal taut wire *W* whose degree of torsion can be controlled by an adjustable screw at the far end and by an adjustable pointer carrying a vernier at the dial end *A*. A beam *B*, hooked at one end, is fixed rigidly to the wire and at right angles to it. The instrument is fitted with adjustable stops *C*, which limit the movement of the beam and also a device for ascertaining whether the beam is in a horizontal plane. A desirable addition for controlling the movement of the beam is a dashpot. The platform *D*, whose height can be adjusted by means of a screw *E*, carries the dish of liquid under examination and is located beneath the hooked end of the beam.

(*b*) *Glass Plate* (Fig 1)—rectangular in shape with a hooked glass rod attached. The plate * should be about 20 mm in length, about 10 mm in width, and about 0·1 mm in thickness. One end of a thin zig-zag glass rod of about 1 mm dia (not less than 0·8 mm and not more than 1·2 mm) is attached to the centre of the upper edge and the other end is hooked. When suspended freely from the beam by means of the hook the plane of the glass plate should be vertical and its lower edge exactly horizontal as judged by reflection on a mercury surface. Any departure from the above requirements should be corrected by heating the corners of the zig-zag in the rod. The lower edge perimeter should be measured to the nearest 0·1 mm.

(*c*) *Glass Dish*—cylindrical in shape, about 5 cm in diameter and about 2·5 cm deep.†

PREPARATION OF APPARATUS

4. (*a*) Calibrate the torsion balance, after it has been set up and levelled, first adjusting the tension on the wire by means of the tension screw provided at the far end until there is no appreciable sag at the mounting of the beam. Then set the pointer to zero on the dial and adjust the torsion screw at the far end of the wire until the beam is horizontal. (The stops at this stage should be adjusted so as not to impede the movement of the beam about the horizontal.) Suspend a weight, *e.g.* 0·5 g, from the hook of the beam and adjust the position of the pointer until the beam is again horizontal. The load is then exactly balanced by the torsion on the wire. Note the dial reading.

(*b*) Calculate the pull in dynes per scale division on the dial from the formula:

$$D = Wg/N$$

where D is the pull in dynes corresponding to one scale division;
W is the load on the hook of the beam in g;
g is the acceleration due to gravity in cm/sec²;
N is the dial reading in number of scale divisions.

(*c*) Clean the glass plate and dish with benzene, acetone, distilled water, and chromic acid in that order. (The chromic acid must be prepared by adding carefully to a hot saturated

* A microscope cover-slip, cut to the required size, will normally be suitable.

† These dimensions are minimum ones, chosen so that the amount of sample needed is kept as small as possible. The limiting factor with respect to the diameter is that the sides of the glass plate must be well clear of the dish-walls, otherwise "end" errors occur. Furthermore, the depth of the oil phase must be greater than the height of the glass plate if buoyancy errors are to be avoided.

solution of potassium dichromate ten times its volume of conc sulphuric acid, and the plate must be immersed in this solution for at least ½ hour at 50°–60° C.) Then wash free from acid with redistilled water * and dry in an oven reserved solely for this purpose. Do not touch the inside of the dish or the glass plate with the fingers.

(*d*) Check the calibration of the instrument, the cleanliness of the glass plate and dish, and the purity of the distilled water by determining the surface tension of the distilled water by the procedure described in Section 5. The true value is 72·8 dynes/cm at 20° C, but in practice values of 71–73 dynes/cm may be taken as satisfactory.

METHOD A—SURFACE TENSION

PROCEDURE

5. (*a*) Ensure that the ambient temperature is between 15° and 25° C. Adjust the instrument as described in Section 4 (*a*) so that the beam is horizontal and the pointer reads zero on the dial. Suspend the glass plate from the hook of the beam and adjust the torsion screw at the far end of the torsion wire until the beam is again horizontal, the dial reading still being zero. Adjust the stops so that the beam rests on the lower stop and the upper stop is in such a position that the beam can be raised no more than is necessary to ensure that it is free to move upwards. Move the pointer so that the beam bears down slightly on the lower stop.

(*b*) Fill the dish to a depth of about 1 cm with the liquid under test, previously adjusted to a temperature of 20° C. Place it on the platform and raise it until the liquid level is about half a centimetre below the lower edge of the glass plate. Adjust the position of the dish on the platform so that the plate hangs centrally above it. Then raise the liquid level by means of the screw *E* until the lower edge of the glass plate just touches the liquid surface. Increase the torsion on the wire by means of the pointer adjustment until the end of the beam just rises from the lower stop. Record the dial reading.

CALCULATION AND REPORTING

6. (*a*) Calculate the surface tension from the following formula:

$$Y = RD/P$$

where Y is the surface tension in dynes/cm;
R is the dial reading in scale divisions;
D is the pull in dynes per scale division (Section 4 (*b*));
P is the perimeter in centimetres of lower edge of the plate (measured to the nearest 0·01 cm).

(*b*) Report the results to the nearest first place of decimals in units of dynes/cm as the surface tension.

PRECISION

7. If the surface tension does not alter with time, results of duplicate tests should not differ by more than the following amount:

Repeatability	*Reproducibility*
1 dyne/cm	2 dynes/cm

METHOD B—INTERFACIAL TENSION BETWEEN WATER AND OIL

PROCEDURE

8. (*a*) Follow the procedure given under 5 (*a*) with the exception that the pointer is set to read † 15·0 on the dial: the glass plate is balanced in air at this setting by adjusting the screw at the far end.

(*b*) Fill the dish to a depth of about 1 cm with redistilled water. Check the purity of the water, the cleanliness of the plate ‡ and dish, and the correctness of the instrumental adjustments by determining the surface tension of the water at 20° C according to Method A. Note that R in 6 (*a*) is now the final dial reading minus 15·0. If the surface tension of water as determined lies between the values 71 and 73 dynes/cm proceed with the next step. If values outside these limits are obtained they are indicative of an improper adjustment or calibration of the tensiometer or of the use of imperfectly cleaned glassware or contaminated water. These possibilities must be investigated in turn until the figure for the surface tension of distilled water lies within the specified limits.

(*c*) Return the pointer to a dial reading less than 15·0. Make sure that the beam is bearing down on the lower stop and that the lower edge of the glass plate is in the surface of the water.

(*d*) Remove any sludge present in the oil sample either by decanting or by centrifuging and then pour the sludge-free oil (adjusted to 20° C) down the side of the dish to form a layer 14 cm deep. This operation should be performed carefully so as to cause the minimum of disturbance to the interface and lower edge of the glass plate.† Note the time to the nearest second at which pouring commenced. Allow the oil–water interface to age for 30 ± 1 seconds and then increase the torsion on the wire by adjusting the pointer at the dial until the beam just rises from the lower stop. Time the above operation so that the measurement is completed in 60 ± 5 seconds after the commencement of pouring the oil sample. Note the time to the nearest second and the dial reading. If the timing is outside of 60 ± 5 seconds proceed to the next step.

(*e*) Turn the pointer to a lower reading so that the beam bears down on the lower stop and then increase the torsion on the wire by adjusting the pointer until the beam just rises from the lower stop. Note the time to the nearest second and the dial reading.

(*f*) Repeat procedure 8 (*e*) at intervals so as to obtain five readings at about 1, 3, 7, 15, and 23 minutes after the commencement of pouring the sample. Plot the readings against the logarithm of time on semi-log paper and obtain the one minute dial reading by extrapolating the line which passes through or close to at least four of the plottings.

(*g*) Remove the glass plate, clean it and dry it according to procedure 4 (*c*), and then suspend it from the hook of the beam. Return the pointer to zero on the dial and raise the platform until the plate is completely immersed in the oil phase in a central symmetrical position so that it is clear of both the surface of the oil and the oil–water interface by about 2 mm as in location (ii) in Fig 1. Increase the torsion on the wire by adjusting the pointer until the beam just rises from the lower stop. Note the dial reading.

CALCULATION AND REPORTING

9. (*a*) Calculate the interfacial tension from the following formula:

$$Y_{ow} = RD/P$$

where Y_{ow} is the interfacial tension of oil–water in dynes/cm;
R is the one minute dial reading according to 8 (*d*) or 8 (*f*) minus the dial reading according to 8 (*g*);
D is the pull in dynes corresponding to one scale division (Section 4 (*b*));
P is the perimeter of the lower edge of the plate (Section 6 (*a*)).

(*b*) Report the results to the nearest first place of decimals in units of dynes/cm as the interfacial tension.

---

* The water used should be twice distilled, the second time from alkaline potassium permanganate. (Tap water must not be used at any stage.)

† This reading or any suitable reading is used to ensure that the glass plate when balanced in oil will give a reading on the scale.

‡ If the glass plate has not been thoroughly cleaned, it will not wet properly and there will be a distortion of the surface at the interface, which presents a "ragged" appearance. In this case the plate must be recleaned and the determination repeated.

PRECISION

10. Results of duplicate tests should not differ by more than the following amount:

Repeatability	*Reproducibility*
2 dynes/cm	4 dynes/cm

ACKNOWLEDGMENTS

The authors wish to thank the Directors of "Shell" Research Ltd, and the director and the manager of the Research Department of Metropolitan-Vickers Electrical Co. Ltd for permission to publish this paper.

References

[1] "Symposium on Insulating Oils," *Bull. Amer. Soc. Test. Mat.*, 1947, **146**, 90.
[2] "Standard Methods for Testing Petroleum and its Products," 16th ed. London: Institute of Petroleum, 1957.
[3] "ASTM Standards on Petroleum Products and Lubricants." Philadelphia: American Society for Testing Materials, 1955.
[4] Andreas, Hauser, and Tucker. *J. Phys. Chem.*, 1938, **42**, 1001.

OBITUARY

R. M. JOHNSON

R. M. JOHNSON, who was killed in an air crash near Chittagong in East Pakistan on 1 July 1957 while on a routine visit to Dacca, had been a member of the Burmah Oil Company since 1938 and was at the time of his death manager of the Trading Company in Chittagong. He had seen service with the Company in India, Pakistan, and Burma and was a much liked and respected member of the managerial staff. His loss is a sad blow to the Company, and those of us who knew him have lost a good friend. All members of the Company, from the highest to the humblest, who had ever come into contact with him grew quickly to like him, and many were the expressions of sympathy received from those in Burma, Pakistan, and India. He had spent much of the last few years in Burma and would have been returning to Rangoon after his assignment in Chittagong. He leaves a widow and two boys of school age. E. D. R.

THE SEPARATION OF MIXTURES OF BIPHENYL, *CYCLO*-HEXYLBENZENE, AND BI*CYCLO*HEXYL BY VAPOUR-PHASE CHROMATOGRAPHY

By W. J. HENDRIKS†, R. M. SOEMANTRI†, and H. I. WATERMAN† (Hon. Fellow)

SUMMARY

The separation of mixtures of biphenyl, *cyclo*hexylbenzene, and bi*cyclo*hexyl by gas–liquid partition chromatography is described. The method of calibration and the quantitative interpretation of the chromatograms are described extensively. The correction factors found are correlated to those found in the system: naphthalene, tetralin, and decalin.

The physical meaning and the relation between the correction factor and the thermal conductivity is described.

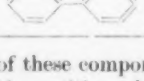
The quantitative separation of six-component mixtures containing biphenyl, *cyclo*hexylbenzene, bi*cyclo*hexyl, naphthalene, tetralin, and decalin is illustrated.

The chromatographic columns used were: dioctylphthalate on firebrick and silicon 702 on Celite. The stability of the columns is discussed.

INTRODUCTION

THE intention is to study the quantitative separation of mixtures of biphenyl, *cyclo*hexylbenzene, and bi*cyclo*hexyl for the analysis of the products, obtained in continuous dehydrogenation and hydrogenation studies with these compounds.

Table of Components

	m.w.	b.p. 760 mm Hg
Bi*cyclo*hexyl	166·30	235° C
*cyclo*Hexyl-benzene	160·25	238° C
Biphenyl 	154·20	255° C

Mixtures of these components have been subjected to gas–liquid partition chromatography, and it is shown that this method offers an excellent quantitative separation of the components mentioned above.

This simple, rapid, and accurate method, for which only very small samples are required, offers great advantages over other analytical methods, such as analytical distillation and ultra-violet and infra-red spectroscopy.

EXPERIMENTAL PART

(1) For the principle of the method and the description of the apparatus and other experimental details, one is referred to the paper by the same authors published earlier.[1]

(2) *The Chromatographic Columns and Operating Variables*

Two chromatographic columns were used for the analyses:

(*a*) dioctylphthalate on ground firebrick;
(*b*) silicon 702 on Celite;

6 mm in diameter and 180 cm in length.[1]

The operating temperatures were 180° and 190° C. Too high temperatures have to be avoided for the same reason as described in reference.[1]

In all analyses *no dehydrogenation* was observed.

The Stability of the Columns. After some orientating experiments to find the most suitable conditions for this separation, the analyses of the mixtures were carried out continuously. The chromatographic column was thus subjected day and night to these severe conditions. After about 50 hours the first symptoms of decline in separating efficiency could be observed, and after about 60 hours the separating efficiency of the columns had declined so much that they could be used no more for this purpose.

This decline in separating efficiency of the chromatographic column is caused by the fact that at these high temperatures the immobile phase is stripped away by the carrier gas, owing to its high vapour-pressure. By this decrease of the amount of the immobile phase the retention times of the components become smaller.

Some investigators indeed use small amounts of immobile phase (15–20 wt %) in order to shorten the time of analysis and to improve the separation.[2]

If, however, the amount of the immobile phase is too small, the separating efficiency decreases sharply.

(3) *The Analyses*

As is shown earlier [1] in the case of the separation of naphthalene, tetralin, and decalin, the areas of the peaks are not directly proportional to the mol-concentrations of the corresponding components in using N_2 as carrier gas. An analogous case is to be expected in the separation of these mixtures of biphenyl, *cyclo*hexylbenzene, and bi*cyclo*hexyl. Several binary mixtures of biphenyl and bi*cyclo*hexyl, biphenyl and *cyclo*hexylbenzene, *cyclo*hexylbenzene and bi*cyclo*hexyl, and ternary mixtures of these three components were accurately prepared in the most

* MS received 21 March 1957.

† University of Chemical Engineering, Delft, Holland.

varying mol ratios. Every component is first tested for purity.

As some mixtures were liquid and others were solid–liquid, a roughly known amount of purified benzene was added to all mixtures, in order to get homogeneous liquid mixtures. The roughly known amount of benzene added is of practical use in order to be able to inject samples that will give chromatograms of the same order of size so that the accuracy of the measuring of the peak areas is the same.

The carrier gas used is again N_2 and the peak areas are taken as the product of the height and the half-band width of the peak.

(4) *Method of Calibration and Results*

In the case of the quantitative separation of the system naphthalene–tetralin–decalin [1] the correction factors for the areas of the peaks of the chromatograms were determined by means of measurement of the chromatograms of equimolar mixtures of, respectively, tetralin and naphthalene and tetralin and decalin.

The method used here is principally the same, but it is extended in order to improve the accuracy :

(*a*) The correction factor for biphenyl is taken as 1. This choice is of course quite arbitrary : *cyclo*hexylbenzene or bi*cyclo*hexyl can also be taken as 1.

(*b*) The determination of the correction factor (α) of *cyclo*hexylbenzene is carried out as follows : for a binary mixture of biphenyl and *cyclo*hexylbenzene—

The mol % *cyclo*hexylbenzene

$$= \frac{\alpha_{ChBz} \cdot A_{ChBz}}{\alpha_{ChBz} \cdot A_{ChBz} + 1 \cdot A_{BPh}} \cdot 100\%$$

The mol % biphenyl

$$= \frac{1 \cdot A_{BPh}}{\alpha_{ChBz} \cdot A_{ChBz} + 1 \cdot A_{BPh}} \cdot 100\%$$

In which A = peak area ;
BPh = biphenyl ;
$ChBz$ = *cyclo*hexylbenzene ;
Bch = bi*cyclo*hexyl.

Thus $$\alpha_{ChBz} = \frac{\text{mol \% } ChBz}{\text{mol \% } BPh} \cdot \frac{A_{BPh}}{A_{ChBz}} \quad . \quad . \quad (1)$$

As the mol ratios of the mixtures are known from the preparation and the peak areas can be measured on the chromatograms, α_{ChBz} can be determined with formula (1). The average value found for $\alpha_{ChBz} = 1{\cdot}20$. With these correction factors $\alpha_{BPh} = 1$ and $\alpha_{ChBz} = 1{\cdot}20$ the chromatograms of these binary mixtures were calculated. The result is shown in Table I.

(*c*) The correction factor of bi*cyclo*hexyl is determined in the same way as for *cyclo*hexylbenzene, with binary mixtures of biphenyl and bi*cyclo*hexyl.

The average value found for $\alpha_{Bch} = 1{\cdot}35$. This value is used in calculating the chromatograms of these binary mixtures. See Table II.

TABLE I

*System : Biphenyl–cyclo**Hexylbenzene*

Number of mixture	Mol %				
	Biphenyl		*cyclo*Hexylbenzene		
	Found	Calc	Found	Calc	Δ
9	46·5	48·6	53·5	51·4	+2·1
10	76·4	75·8	23·6	24·2	−0·6
11	26·3	26·4	73·7	73·6	+0·1
12	91·7	91·2	8·3	8·8	−0·5
13	12·2	11·6	87·8	88·4	−0·6

Δ average : 0·8% Δ maximum : 2·1%
Δ = (mol % found)–(mol % calculated)

TABLE II

*System : Biphenyl–Bicyclo**hexyl*

Number of mixture	Mol %				
	Biphenyl		Bi*cyclo*hexyl		
	Found	Calc	Found	Calc	Δ
4	52·3	53·2	47·7	46·8	+0·9
5	26·9	27·2	73·1	72·8	+0·3
6	76·9	75·8	23·1	24·2	−1·1
7	96·3	95·95	3·7	4·05	−0·4
8	10·7	9·05	89·3	90·95	−1·7

Δ average : 0·9% Δ maximum : 1·7%
Δ = (mol % found)–(mol % calculated)

(*d*) Thus the three correction factors are—

$\alpha_{BPh} = 1$ (by definition)
$\alpha_{ChBz} = 1{\cdot}20$
$\alpha_{Bch} = 1{\cdot}35$

To test these determined α-values, they are applied to the chromatograms of binary mixtures of *cyclo*hexylbenzene and bi*cyclo*hexyl, and to ternary mixtures of biphenyl, *cyclo*hexylbenzene, and bi*cyclo*hexyl, the results of which are shown in Tables III and IV.

TABLE III

System : cyclo*Hexylbenzene–Bicyclo**hexyl*

Number of mixture	Mol %				
	*cyclo*Hexylbenzene		Bi*cyclo*hexyl		
	Found	Calc	Found	Calc	Δ
14	48·7	47·7	51·3	52·3	−1·0
15	76·8	75·2	23·2	24·8	−1·6
16	24·7	25·5	75·3	74·5	+0·8
17	90·0	90·7	10·0	9·3	+0·7
18	11·9	11·3	88·1	88·7	−0·6

Δ average : 0·9% Δ maximum : 1·6%
Δ = (mol % found)–(mol % calculated)

TABLE IV

*System: Biphenyl, cyclo*Hexylbenzene, *Bicyclohexyl*

Number of mixture	Mol %								
	Biphenyl			*cyclo*Hexylbenzene			Bicyclohexyl		
	Found	Calc	Δ	Found	Calc	Δ	Found	Calc	Δ
19	34·4	35·5	−1·1	31·4	32·8	−1·4	34·2	31·7	+2·5
20	49·9	51·6	−1·7	25·2	24·4	+0·8	24·9	23·9	+1·0
22	39·1	41·5	−2·4	22·4	19·4	+3·0	38·5	39·1	−0·6
23	25·2	26·3	−1·1	51·5	49·4	+2·1	23·3	24·3	−1·0
24	40·0	40·6	−0·6	42·4	39·6	+2·8	17·6	19·9	−2·3
25	18·9	18·9	0·0	42·1	43·0	−0·9	39·0	38·1	+0·9
26	4·3	4·3	0·0	47·2	48·0	−0·8	48·5	47·7	+0·8
28	50·0	49·6	+0·4	47·0	46·5	+0·5	3·0	3·9	−0·9
29	13·1	12·2	+0·9	33·7	33·3	+0·4	53·1	54·5	−1·4
31	56·2	55·6	+0·6	35·1	34·1	+1·0	8·7	10·3	−1·6
32	42·3	44·3	−2·0	15·9	14·6	+1·3	41·8	41·1	+0·7
33	36·9	35·6	+1·3	55·6	55·4	+0·2	7·5	8·9	−1·4
Δ maximum			2·4			3·0			2·5
Δ average			1·0			1·3			1·3

Δ = (mol % found)–(mol % calculated)

These tables show clearly that the determined α-values for bi*cyclo*hexyl and *cyclo*hexylbenzene are correct.

(*e*) In the system naphthalene, tetralin, and decalin, the correction factors found were as follows: [1]

$$\alpha_N = 1/1{\cdot}3$$
$$\alpha_T = 1 \text{ (by definition)}$$
$$\alpha_D = 1{\cdot}07$$

In order to have a correlation between this system and the system biphenyl–*cyclo*hexylbenzene–bi*cyclo*hexyl, the correction factor of naphthalene (α_N) with respect to biphenyl is determined with binary mixtures of biphenyl and naphthalene, in the way as described under (*b*).

The average value found for $\alpha_N = 1{\cdot}60$. This value, applied for the calculation of the chromatograms of these binary mixtures, gives the results as shown in Table V.

TABLE V

System: Biphenyl–Naphthalene

Number of mixture	Mol %				
	Biphenyl		Naphthalene		
	Found	Calc	Found	Calc	Δ
41	43·7	43·55	56·3	56·45	−0·2
42	26·0	25·8	74·0	74·2	−0·2
43	59·1	59·7	40·9	40·3	+0·6
44	13·7	12·8	86·3	87·2	−0·9
45	66·5	66·65	33·5	33·3	+0·2

Δ average: 0·4% Δ maximum: 0·9%
Δ = (mol % found)–(mol % calculated)

(*f*) The correction factor of naphthalene (α_N) being 1·60, the correction factors of tetralin and decalin become respectively:

$$\alpha_T = 1{\cdot}60 \times 1{\cdot}3 \rightarrow \alpha_T = 2{\cdot}10$$
$$\alpha_D = 1{\cdot}60 \times 1{\cdot}3 \times 1{\cdot}07 \rightarrow \alpha_D = 2{\cdot}20$$

For the six-component system: biphenyl–*cyclo*hexylbenzene–bi*cyclo*hexyl–naphthalene–tetralin–decalin, the correction factors are shown in the table below.

Table of Correction Factors

$\alpha_{BPh} = 1$	$\alpha_{Bch} = 1{\cdot}35$	$\alpha_T = 2{\cdot}10$
$\alpha_{ChBz} = 1{\cdot}20$	$\alpha_N = 1{\cdot}60$	$\alpha_D = 2{\cdot}20$

(*g*) In applying these correction factors to binary mixtures of

biphenyl–decalin
biphenyl–tetralin
*cyclo*hexylbenzene–decalin
*cyclo*hexylbenzene–tetralin
*cyclo*hexylbenzene–naphthalene
bi*cyclo*hexyl–decalin
bi*cyclo*hexyl–tetralin
bi*cyclo*hexyl–naphthalene

the α-values prove to be correct.

The results are shown in Table VI.

TABLE VI

System	Number of mixture	Mol %				
		Highest boiling component		Lowest boiling component		
		Found	Calc	Found	Calc	Δ
Biphenyl–tetralin	55	42·8	45·0	57·2	55·0	+2·2
Biphenyl–decalin	56	51·6	49·9	48·4	50·1	−1·7
*cyclo*Hexylbenzene–naphthalene	52	44·9	43·7	55·1	56·3	−1·2
*cyclo*Hexylbenzene–tetralin	53	43·6	45·0	56·4	55·0	+1·4
*cyclo*Hexylbenzene–decalin	54	48·5	49·6	51·5	50·4	+1·1
Bi*cyclo*hexyl–naphthalene	50	45·4	42·8	54·6	57·2	−2·6
Bi*cyclo*hexyl–tetralin	51	27·3	29·4	72·7	70·6	+2·1
Bi*cyclo*hexyl–decalin	49	46·7	46·5	53·3	53·5	−0·2

Δ = (mol % found)–(mol % calculated)

A correlation is thus made between these two systems.

(*h*) As an illustrative example, the analyses of six-component mixtures consisting of all the components mentioned above are shown in Table VII.

TABLE VII

*System: Biphenyl–*cyclo*Hexylbenzene–Bi*cyclo*hexyl–Naphthalene–Tetralin–Decalin*

Number of mixture		Mol %					
		Biphenyl	*cyclo*-Hexylbenzene	Bicyclohexyl	Naphthalene	Tetralin	Decalin
46	Found	11·8	13·8	12·4	25·5	21·6	14·8
	Calc	14·1	14·7	13·5	23·55	18·9	15·25
	Δ	−2·3	−0·9	−1·1	+2·0	+2·7	−0·5
60	Found	20·8	22·3	20·6	7·4	5·7	23·1
	Calc	22·0	21·6	21·1	6·9	6·6	21·8
	Δ	−1·2	+0·7	−0·5	+0·5	−0·9	+1·3

Δ = (mol % found)–(mol % calculated)

Herewith is shown the possibility and accuracy of the quantitative separation of mixtures of these high-boiling, some of which are close-boiling, components by gas–liquid partition chromatography.

Note: In the determination of the correction factors α_{ChBz}, α_{Bch}, and α_N, as shown in Tables I, II, and V, the results were obtained in practically all cases from at least two chromatograms per mixture. For practically all other mixtures only one chromatogram per mixture is used for the determination of the composition.

DISCUSSION OF THE RESULTS

As can be seen from Tables I–V, this method of calibration results in an average accuracy of the analyses of ±1 per cent absolute. The maximum deviation observed in all analyses was 3 per cent absolute.

It is remarkable that the highest-boiling components in the systems biphenyl–*cyclo*hexylbenzene–bi*cyclo*hexyl and naphthalene–tetralin–decalin respectively, which are both total aromatics, have the smallest correction factor. The lowest-boiling components, both totally saturated, have the highest correction factor.

These results suggest a certain relationship between the type of hydrocarbon and the correction factor or thermal conductivity.

For an understanding of the physical meaning of the correction factor, the response of the thermal conductivity cell to the signals, caused by the change in the composition of the effluent gas stream, must be considered. See Fig 1. The signal is thus the difference between the thermal conductivity of pure N_2 and the thermal conductivity of a mixture of N_2 and a component. Thus the same mol concentration of biphenyl, *cyclo*hexylbenzene, or bi*cyclo*hexyl in the effluent gas stream gives rise to different signals in the katharometer, owing to its mutual difference in thermal conductivity.

Assuming proportionality of the response to the signal, then α_{ChBz} is proportional to the ratio a/b and α_{Bch} to the ratio a/c. It means that the higher the thermal conductivity of a component, the greater the correction factor (α).

In using H_2 or He as carrier gas, which have thermal conductivity eight times as high as N_2, the situation is given in Fig 1. It can readily be seen that the α-values will be smaller and are nearly equal to 1. That is why for most purposes it is not necessary to carry out calibration to determine the correction factors of the several components in using H_2 as carrier gas.[3] For accurate work and for components mutually differing very much in thermal conductivity, it is yet necessary to carry out calibrations to determine the α-values.

In this method to every component an average α-value is given, as determined from the chromatograms of known mixtures. That means that α is considered to be concentration-independent. This is strictly only correct in assuming the lines, connecting the λ_{N_2} and $\lambda_{comp.}$ (Fig 1) to be straight: the thermal

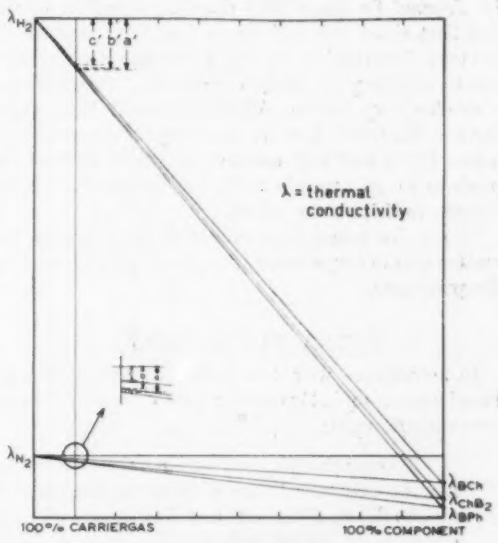


FIG 1

THE SIGNAL CORRESPONDING TO BIPHENYL IS *a*, TO *cyclo*HEXYLBENZENE *b*, AND TO BI*cyclo*HEXYL *c*, FOR THE SAME MOL CONCENTRATIONS OF THESE COMPONENTS IN THE EFFLUENT GAS STREAM

conductivity of mixtures of N_2 and a component varies linearly with the concentration of that component in the N_2 gas. If these lines are curved, then α will be a function of the concentration.

However, considering the fact that the vapour concentration of a component in the carrier gas is usually very small, it is quite justifiable to consider the lines to be straight in this small interval. With this assumption the use of one value of α for a component is justified.

ACKNOWLEDGMENT

The authors are indebted to E. C. Wessels for his assistance in the experimental part.

References

1 Soemantri, R. M., and Waterman, H. I. *J. Inst. Petrol.*, 1957, **43**, 94–9.
2 van der Craats, F. *Analyt. Chim. Acta.*, 1956, **14**, 126.
3 Phillips, C. "Gas Chromatography." London: Butterworths, 1956.

REPORT OF IP CARBON RESIDUE PANEL *

INTRODUCTION

It will be recalled that a notice was inserted in the *IP Journal* for June 1954 drawing attention to the fact that since 1947 a footnote had been included in the text of method IP 13 urging that the Ramsbottom test be used in place of the Conradson. This followed a similar step by the ASTM in 1946. The notice further indicated that it was hoped ultimately to delete IP 13 and that endeavours would be made to produce an acceptable table for converting Ramsbottom to Conradson values.

The notice asked for views of those to whom this matter was of importance, but the response was very disappointing.

FORMATION OF PANEL

In accordance with the above, a Carbon Residue Panel was set up in September 1954 with the following terms of reference:

> "To examine the conversion tables which are now in existence to see if either is suitable. If not, to devise a new one and then to examine the question of the recommendation that IP 13 be deleted from *Standard Methods*, provision being made for the conversion of Ramsbottom results to Conradson values by the use of that table."

PANEL ACTIVITIES

Preliminary Work

As a first step it was felt that the information on which the ASTM correlation had been based should be examined, since it did not appear to agree altogether with results obtained in the U.K. These data were later obtained and examined, together with experimental results on fuels, fuel 10 per cent bottoms, and lubricating oils provided by seven U.K. laboratories. In all, about 150 determinations by each method were made available from U.K. and 120 from ASTM sources. Consideration of these results led to the following conclusions:

(1) The results of four of the seven U.K. laboratories satisfied a single correlation (see Fig 1) given by the following equation:

$$R = 0{\cdot}777 + 0{\cdot}403C + 0{\cdot}105C^2 \quad . \quad (1)$$

when $R = \log_{10}$ (100 × Ramsbottom result %), and $C = \log_{10}$ (100 × Conradson result %). This equation is based on results for the whole fuel, but statistically there was no reason to believe that the 10 per cent bottoms were represented by a different equation. It applied only above a Conradson carbon residue level of 0·1 per cent. Below this level any correlation had little meaning due to the steepness of the curve and to the wide spread of results.

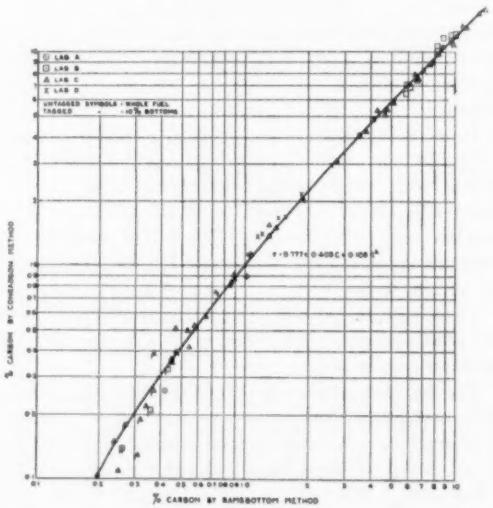


Fig 1

IP CORRELATION DATA. LABORATORIES A, B, C, AND D

(2) The results from the remaining three U.K. laboratories satisfied a quite different correlation (Fig 2).

(3) There was insufficient data from the lubricating oils examined in the U.K. (those results reported by lab 7) to show whether the systematic differences of these results from the curve represented by the above equation were due to systematic laboratory error, or to a systematic difference due to the fact that the measurements were on lubricating oils.

(4) The ASTM data (Fig 3) had a spread about the best curve through them greater than that shown by the four laboratories mentioned above and comparable to the total spread of results given in the IP investigation.

(5) The ASTM data represented a significantly different correlation from the one established above, and 85 per cent of the ASTM results lie above the smooth curve shown in Fig 1. This is

* MS received 15 May 1957.

also indicated in Fig 4, which shows the ASTM correlation curve drawn through the U.K. results, and in Fig 5, which shows both correlation curves and all U.K. and ASTM results.

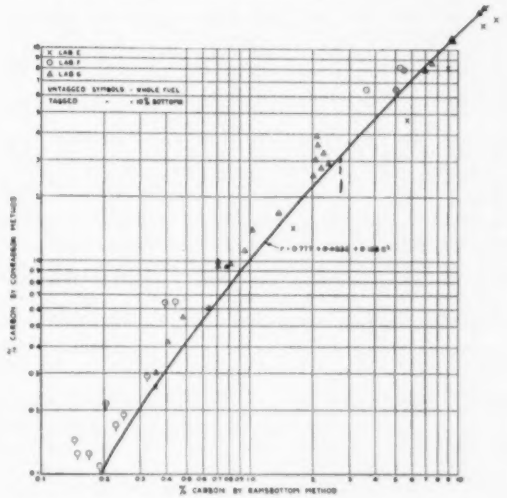


FIG 2

IP CORRELATION DATA. LABORATORIES E, F, AND G

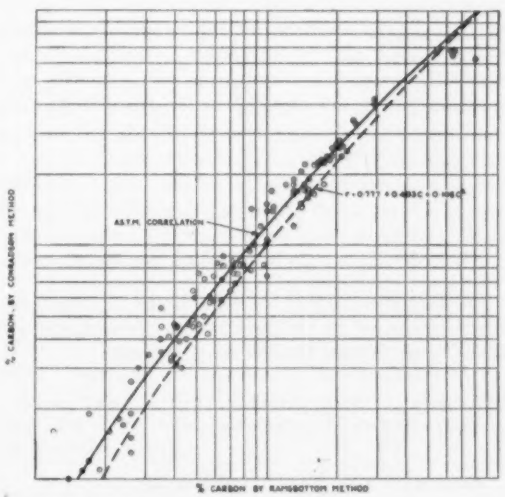


FIG 3

ASTM CORRELATION DATA
(showing IP Correlation Curve)

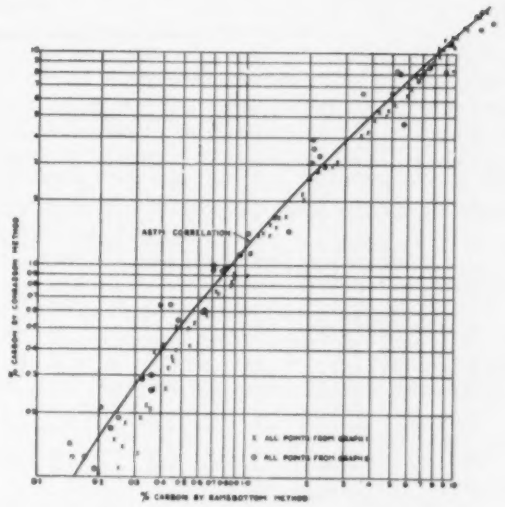


FIG 4

ALL U.K. RESULTS, WITH ASTM CORRELATION LINE

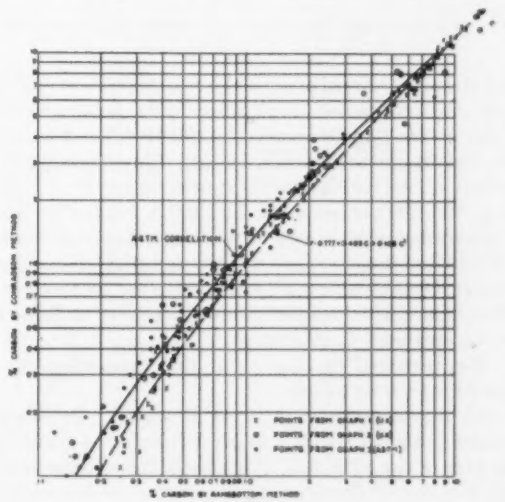


FIG 5

U.K. AND ASTM RESULTS, WITH ASTM AND U.K. CORRELATION LINES

Co-operative Testing Programme

As regards (2) above, it was not possible, from the data available, to say whether the three laboratories differed in respect of their Conradson or their Ramsbottom results, or purely on account of different types of oil being tested at each centre. In view of this and other uncertainties, it was decided to carry out a co-operative programme of tests designed statistically to give the following information:

(1) Those laboratories that were giving results by either method of test systematically different from those of the other laboratories.

(2) The repeatability and reproducibility of each method of test.

(3) Whether separate correlations were required for whole fuels, 10 per cent bottoms (fuels), and lubricating oils.

It was proposed to re-examine the correlation data already analysed in the light of these results. Ten

TABLE I

Experimental Results Obtained in Correlation Programme

Laboratory	Conradson residues, wt %										Ramsbottom residues, wt %									
	Fuel 1	Fuel 2	Fuel 3	Fuel 4	Btms 1	Btms 2	Lub. oil 1	Lub. oil 2	Lub. oil 3	Lub. oil 4	Fuel 1	Fuel 2	Fuel 3	Fuel 4	Btms 1	Btms 2	Lub. oil 1	Lub. oil 2	Lub. oil 3	Lub. oil 4
A	0·17	0·46	1·30	8·58	0·10	0·41	0·09	0·45	1·38	7·82	0·25	0·57	1·27	7·50	0·22	0·47	0·15	0·33	1·07	6·92
	0·17	0·47	1·33	8·58	0·10	0·41	0·09	0·50	1·43	7·64	0·24	0·58	1·25	7·46	0·22	0·47	0·15	0·35	1·08	6·83
B	0·16	0·47	1·24	8·49	0·11	0·42	0·11	0·45	1·53	7·70	0·20	0·52	1·00	7·25	0·20	0·40	0·14	0·27	0·89	6·90
	0·16	0·52	1·26	9·18	0·14	0·44	0·11	0·45	1·57	7·70	0·23	0·53	1·00	7·30	0·21	0·43	0·12	0·28	0·89	6·90
C	0·17	0·48	1·28	8·13	0·13	0·43	0·12	0·43	1·52	7·71	0·30	0·58	1·30	7·52	0·23	0·47	0·17	0·41	1·19	6·91
	0·18	0·48	1·28	8·26	0·12	0·43	0·14	0·41	1·57	7·82	0·30	0·57	1·28	7·55	0·23	0·48	0·17	0·40	1·19	7·00
D	0·17	0·50	1·24	8·10	0·10	0·34	0·10	0·35	1·56	7·90	0·27	0·54	1·18	6·84	0·21	0·49	0·16	0·32	0·94	6·21
	0·20	0·54	1·28	8·10	0·10	0·35	0·11	0·35	1·48	8·16	0·27	0·53	1·18	6·97	0·20	0·48	0·15	0·50	0·93	6·40
E	0·17	0·45	1·25	8·17	0·12	0·41	0·13	0·61	1·61	7·86	0·27	0·56	1·24	7·67	0·20	0·47	0·18	0·39	0·93	7·05
	0·17	0·46	1·31	8·43	0·12	0·42	0·19	0·50	1·67	7·80	0·27	0·58	1·29	7·59	0·21	0·44	0·17	0·41	0·96	7·04
F	0·19	0·50	1·27	8·29	0·11	0·44	0·12	0·47	1·59	7·85	0·29	0·52	1·11	7·05	0·20	0·45	0·12	0·26	0·85	6·20
	0·20	0·51	1·35	8·48	0·12	0·46	0·15	0·50	1·63	7·94	0·29	0·55	1·12	7·33	0·23	0·47	0·14	0·29	0·94	6·46
G	0·18	0·47	1·35	8·64	0·14*	0·48*	0·15	0·47	1·59	8·10	0·30	0·68	1·27	7·78	0·22*	0·58*	0·16	0·36	1·22	7·20
	0·18	0·49	1·32	8·55	0·13*	0·47*	0·15	0·51	1·59	8·20	0·31	0·67	1·28	7·83	0·21*	0·57*	0·16	0·37	1·22	7·20
H	0·18	0·48	1·38	8·99	0·12	0·29	0·10	0·47	1·40	7·50	0·25	0·59	1·14	6·96	0·21	0·52	0·17	0·36	1·06	6·80
	0·17	0·50	1·39	8·54	0·10	0·30	0·11	0·49	1·43	7·85	0·24	0·57	1·24	7·45	0·20	0·54	0·17	0·38	1·06	6·75
I	0·16	0·46	1·23	8·36	0·13	0·48	0·09	0·40	1·57	7·89	0·26	0·54	1·30	7·61	0·17	0·47	0·17	0·36	1·04	6·90
	0·17	0·49	1·20	8·44	0·10	0·47	0·12	0·38	1·52	7·87	0·27	0·56	1·28	7·66	0·17	0·47	0·15	0·34	1·05	7·01
J	0·19	0·47	1·30	8·80	0·10	0·46	0·10	0·36	1·34	6·63	0·26	0·55	1·18	6·96	0·20	0·43	0·19	0·37	1·02	6·51
	0·17	0·46	1·30	8·60	0·10	0·45	0·10	0·42	1·19	6·58	0·28	0·55	1·20	7·07	0·22	0·41	0·19	0·37	1·04	6·54

* Owing to the fact that these results were obtained at a much later date than those of the other participants, they have not been included in the statistical analysis.

laboratories co-operated in the programme, in which ten oils were tested (duplicates) by each laboratory, both by the Conradson method (IP 13/42) and by the Ramsbottom method (IP 14/45). The ten oils consisted of four fuel oils giving approximately 0·15, 0·45, 1·5, and 8·0 per cent weight carbon residue by the Conradson method; two 10 per cent bottoms at levels of 0·15 and 0·45 per cent weight, and four lubricating oils at levels of 0·15, 0·45, 1·5, and 8·0 per cent weight. The experimental results obtained are given in Table I as an appendix to this report.

The principal findings from this correlation programme were as follows:

(a) *Repeatability of the Two Methods.** Duplicate values obtained simultaneously by the same operator as part of the same test on adjacent sets of apparatus (in the case of the Conradson) or using the same bath (in the case of the Ramsbottom) should not differ by more than the following amounts:

Conradson

Level of lower residue	Fuel oil	Lubricating oil	10% bottoms
0·1	0·02	0·03	0·03
0·2	0·03	0·04	0·03
0·5	0·05	0·05	0·03
1·0	0·08	0·08	—
2·0	0·14	0·12	—
5·0	0·33	0·26	—
10·0	0·63	0·49	—

Ramsbottom

Level of lower residue	Fuel oil and lubricating oil	10% bottoms
0·1	0·01	0·03
0·2	0·02	0·03
0·5	0·03	0·03
1·0	0·05	—
2·0	0·09	—
5·0	0·22	—
10·0	0·42	—

(b) *Reproducibility of the Two Methods.* Duplicate results obtained in different laboratories should not differ by more than the following amounts:

Conradson

Level of lower residue	Fuel oil	Lubricating oil	10% bottoms
0·1	0·03	0·09	0·05
0·2	0·04	0·10	0·10
0·5	0·07	0·14	0·24
1·0	0·11	0·19	—
2·0	0·20	0·31	—
5·0	0·42	0·63	—
10·0	0·82	1·17	—

* The figures given in the tables in this section are not true repeatabilities as defined. They give the maximum difference that should be obtained between duplicate observations in one test. A true repeatability would give the maximum difference between two test results, these being the mean of two observations. The test repeatabilities would be obtained by dividing the terms of these tables by $\sqrt{2}$.

Ramsbottom

Level of lower residue	Fuel oil and lubricating oil	10% bottoms
0·1	0·06	0·03
0·2	0·08	0·05
0·5	0·12	0·13
1·0	0·20	—
2·0	0·34	—
5·0	0·78	—
10·0	1·50	—

It will be seen that the Conradson reproducibility limits were larger than the corresponding repeatability limits, as is usual in most methods of test. It appears from the analysis that this increase is probably not due to general systematic differences between the results from different laboratories, such as may be caused by differences in apparatus and/or technique at the different centres, but is due rather to the long-term variability of the results. However, two particular laboratories showed systematically high or low results on certain types of oil as follows:

Lab. J . . . . Low on lubricating oils
Lab. E . . . . High on lubricating oils

These results were rejected before the reproducibility figures quoted above were calculated.

In the case of the Ramsbottom, reproducibility limits were again larger than the corresponding repeatability limits. However, in addition to the probable long-term variability of the results, there were in general systematic differences between different laboratories in the case of fuels and lubricating oils, but apparently not in the case of 10 per cent bottoms. Such differences have been taken to indicate that the method of test insufficiently specifies the apparatus and/or technique to be used. Again, three laboratories showed abnormally large systematic differences on certain types of oil as follows:

Lab. G . . . High on fuels and lubricating oils
Labs B and F . . Low on fuels and lubricating oils

If the method could be more rigorously specified in order to remove the systematic differences, and assuming that no other changes were to occur, the reproducibility would be improved to approximately the following values:

Level of lower residue	Fuel oil and lubricating oil
0·1	0·04
0·2	0·05
0·5	0·08
1·0	0·12
2·0	0·21
5·0	0·49
10·0	0·94

(c) *Results Using the ASTM Method and Apparatus.* Only one of the participating laboratories, namely, E, used the ASTM method and apparatus in the co-operative tests, but the results did not indicate any undue influence from this source.

(d) *Correlation of Results by the Two Methods of Test.* When the results for each sample were averaged over the ten participating laboratories, the average results on fuels and 10 per cent bottoms were found to fit very closely to equation (1) established previously. It has, however, been found that the best fitting-line can be expressed by a simple linear equation as follows:

$$R = 0{\cdot}133 + 0{\cdot}8397C \quad . \quad . \quad . \quad (2)$$

when R = Ramsbottom result per cent, and
C = Conradson result per cent.

It is of interest to note that the lubricating oil sample showing the highest carbon residue is satisfied

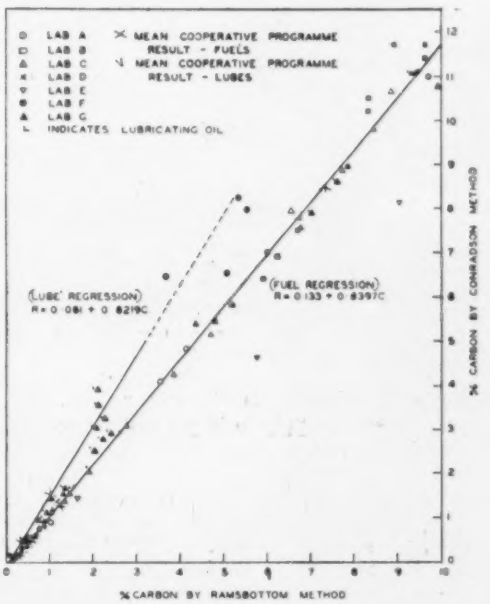


FIG 6

IP CORRELATION DATA—LINEAR PLOT WHOLE FUEL DATA

by the above equation, whereas the remaining three lubricating oil samples show quite a different correlation given by the following equation:

$$R = 0{\cdot}081 + 0{\cdot}8219C \quad . \quad . \quad . \quad (3)$$

Fig 6 shows all the U.K. results on a linear plot in accordance with equations (2) and (3) above, and Fig 7 those of 10 per cent bottoms.

(e) *Confidence Limits on Converted Values.* Estimates of the Ramsbottom carbon residues were obtained from the observed Conradson carbon residue results (*i.e.* the means of pairs of individual experimental determinations) by means of equation (2) above, and this relationship was also used to obtain

estimates of Conradson determinations from the Ramsbottom results.

The table below shows these confidence intervals about the estimated and observed results by both

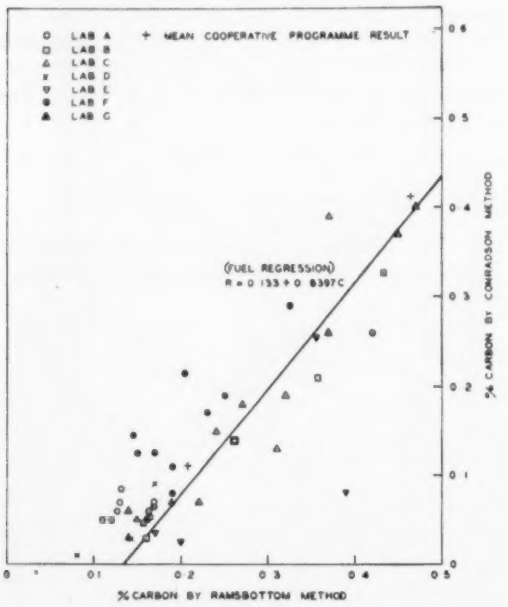


FIG 7

IP CORRELATION DATA—LINEAR PLOT 10 PER CENT BOTTOMS DATA

methods at various levels of carbon residue. These do not necessarily apply to 10 per cent bottoms or to the lubricating oils.

Level, wt %	Observed Conradson results, ±wt %	Estimated Conradson results, ±wt %	Observed Ramsbottom results, ±wt %	Estimated Ramsbottom results, ±wt %
(1)	(2)	(3)	(4)	(5)
0·1	0·02	0·10	0·08	0·08
0·2	0·03	0·10	0·08	0·08
0·5	0·04	0·13	0·11	0·11
1·0	0·07	0·16	0·15	0·15
2·0	0·13	0·24	0·22	0·23
5·0	0·30	0·47	0·45	0·49
10·0	0·59	0·84	0·84	0·92

The results from all ten laboratories have been included in arriving at the above, since to exclude the results from all laboratories with systematic departures in either method of test would have left insufficient data.

The following conclusions can be reached in view of the above figures:

(i) Some of the confidence intervals are wider than is consistent with the reproducibility previously quoted and which had been obtained after omitting data from some laboratories. If the test procedures were specified sufficiently rigorously it is reasonable to suppose that systematic differences between laboratories would be removed, and consequently the confidence limits could be narrowed considerably.

(ii) There is a closer correspondence between columns 4 and 5 of the table than between columns 2 and 3. This is consistent with the finding that the systematic differences between the Ramsbottom determinations of various laboratories were greater than those for Conradson determinations.

MAIN CONCLUSIONS AND RECOMMENDATIONS OF THE PANEL

(1) There is a correlation between Conradson and Ramsbottom results on whole fuels and 10 per cent bottoms which can be represented by

$$R = 0{\cdot}133 + 0{\cdot}8397C$$

when R and C are the Ramsbottom and Conradson carbon residues respectively in per cent by weight.

(2) The above cannot be applied to lubricating oils, and a similar equation for this conversion, but developed on a very small number of oils, is

$$R = 0{\cdot}081 + 0{\cdot}6219C$$

when R and C have the same significance as above.

(3) Both the above are appreciably different from the conversion employed by the ASTM, which is based on both fuels and lubricating oils, although the IP and ASTM curves converge at high carbon residue values. For any given Ramsbottom value, the ASTM chart gives a higher Conradson figure than does the IP.

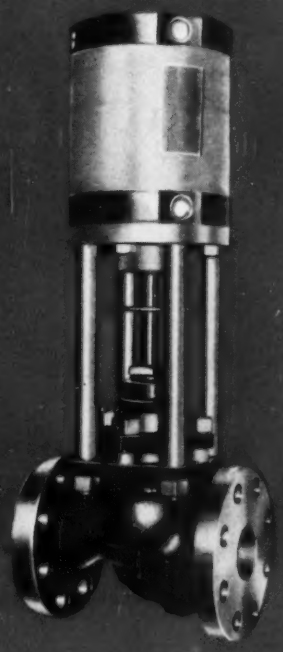
(4) Although the IP work indicates that there is little difference between the confidence which can be placed on determined and calculated Ramsbottom results, more confidence can be placed on determined Conradson values than on those calculated. This is believed to be due to a systematic error in the Ramsbottom method of test greater than any such systematic error in the case of the Conradson.

(5) In view of point (4) above, the Panel recommends that:

(*a*) Their correlation should not be adopted at present.

(*b*) The Conradson test should not be deleted from *Standard Methods*.

(*c*) Efforts should be made to confirm the existence or otherwise of a systematic error in results obtained by the Ramsbottom method of test. If such an error is found, efforts should be made to resolve this by specifying the procedure and/or apparatus more rigorously.



KLINGERMATIC

Klingermatic Valves are ideally suited for remote operation by compressed air or hydraulics for use as control valves on filling lines, process control valves, emergency valves, and similar applications where rapid operation is required.

The construction of the Klingermatic Valve is such that there is no seat to regrind. Perfect tightness is obtained by using resilient Klinger Valve Rings which are closely compressed around a sliding piston.

The valves are available with flanged connections in all sizes from ½" to 8" bore and, in the case of air-operated valves, are designed for use with an air supply at 70 p.s.i.

Write for full details.

Klinger AIR OPERATED VALVES

RICHARD KLINGER LIMITED

Klingerit Works, Sidcup, Kent

Telephone: Foots Cray 7777

G.31/57.KM

I'm fed up with filters!
let's sit down...

Let's sit down and talk about cricket, the weather... anything so long as it isn't your confounded Simmonds Fram Separators.

Sorry old man . . . didn't mean to bore you.

That's quite all right. Delighted to know the R.A.F. is getting up to date. So you actually fly your planes on kerosene now instead of water!

Very comical! Anyway, it's not the whole point. I admit the main object of Simmonds Fram Separators is to remove all the water, but they also take out the solids.

Little strips of erk, for instance?

. . . Anything down to 5 microns.

That gives me a big kick.
Which is more than I can say for this brew . . .

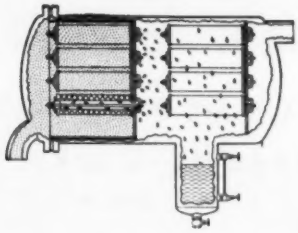
There you are. Now if we could persuade Sally to fit Simmonds Water Separators to the barrels . . .

the point of the argument... **FRAM SEPARATOR FILTERS** for clean water-free fuel

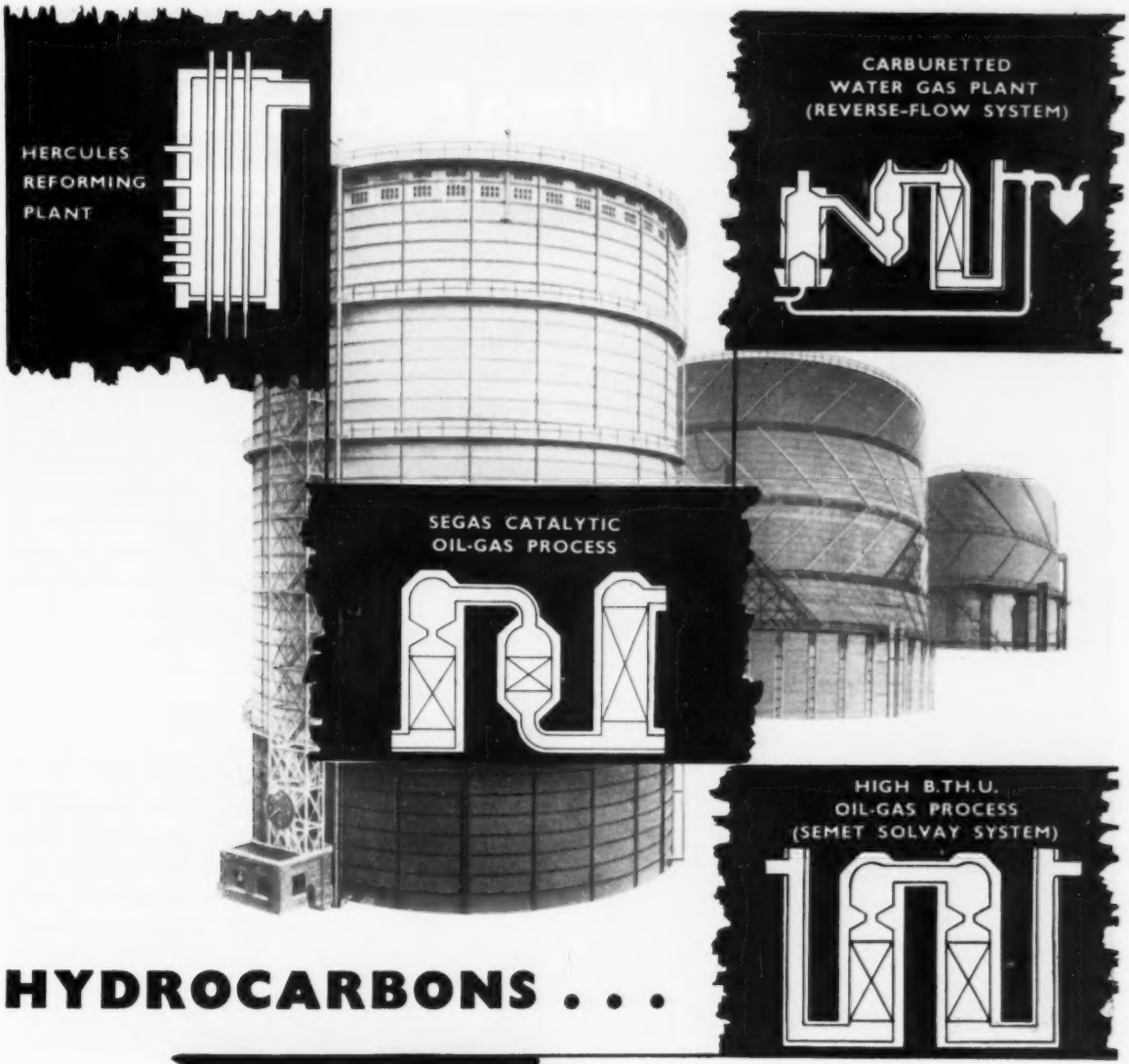
For more details of this and other Simmonds products for the aviation industry **SEND FOR LITERATURE** *to*

SIMMONDS AEROCESSORIES LTD.
Byron House, 7-8-9, St James's Street, London, S.W.1.
Head Office & Works: Treforest, Pontypridd, Glamorgan.
Also Birmingham, Manchester, Glasgow, Stockholm, Copenhagen, Ballarat, Sydney, Johannesburg, Amsterdam and New York.

A MEMBER OF THE FIRTH CLEVELAND GROUP FC



CBC 5WS



HYDROCARBONS . . .

. . . in the service of the Gas Industry

321

THE POWER-GAS CORPORATION LTD

(THE PARENT COMPANY OF THE POWER-GAS GROUP)

STOCKTON-ON-TEES AND LONDON

AUSTRALIA · CANADA · INDIA · FRANCE · SOUTH AFRICA

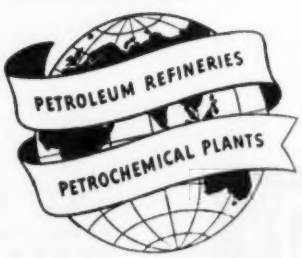
Wrong Place to Cut Costs of a New Process Plant

When building a new process plant, engineering is the easiest place to cut investment costs. But it's the wrong place! The saving of a few hundred hours of engineering, or trying to buy engineering at a price, can cost thousands of extra hours of field labour and additional thousands of pounds for materials. Although the added cost of inadequate engineering seldom can be pin-pointed beforehand, it is inevitably reflected in the operating record of the plant. Better engineering is the basis of the Kellogg organisation's world-wide reputation both as engineers and builders of complete process plants and as consultants on various special engineering projects. This better engineering is the result of good engineers working in an atmosphere where sound engineering is the measure of success for both the individual and the organisation. To Kellogg's clients, better engineering means plants built at the lowest capital investment consistent with reasonable operating and maintenance costs. Kellogg International Corporation welcomes the opportunity to demonstrate how better engineering can benefit companies contemplating new process plants.

Kellogg International Corporation

KELLOGG HOUSE CHANDOS STREET, CAVENDISH SQ. LONDON W.1.

SOCIETE KELLOGG · PARIS
THE CANADIAN KELLOGG COMPANY LTD · TORONTO
KELLOGG PAN AMERICAN CORPORATION · NEW YORK
COMPANHIA KELLOGG BRASILEIRA · RIO DE JANEIRO
COMPANIA KELLOGG DE VENEZUELA · CARACAS



Subsidiaries of
THE M. W. KELLOGG COMPANY
NEW YORK

PRESERVATION

Head of HAMMURABI King of Babylon Circa 1728-1686 *B.C.*

IN THE MIDDLE EAST nature has buried and preserved traces of ancient cities and palaces. The sands of Egypt overwhelmed the Valley of the Kings. Great Empires which once flourished in Mesopotamia were reduced to mysterious mounds in the desert. Huge temples have eroded away while delicate writings on Papyrus have been preserved.

It is a region of violence and contrast, presenting anew to the 20th Century its problems of preservation. Problems not alone of material preservation but in a broader sense—of the preservation of our standards of life.

Fully aware of their responsibility to maintain an invariable standard of preservation inch-by-inch over hundreds of miles of pipeline, many oil Engineers insist on the use of " BITUMASTIC " coatings. The tough proving ground of the Middle East has demonstrated over the years, the wisdom of their choice.

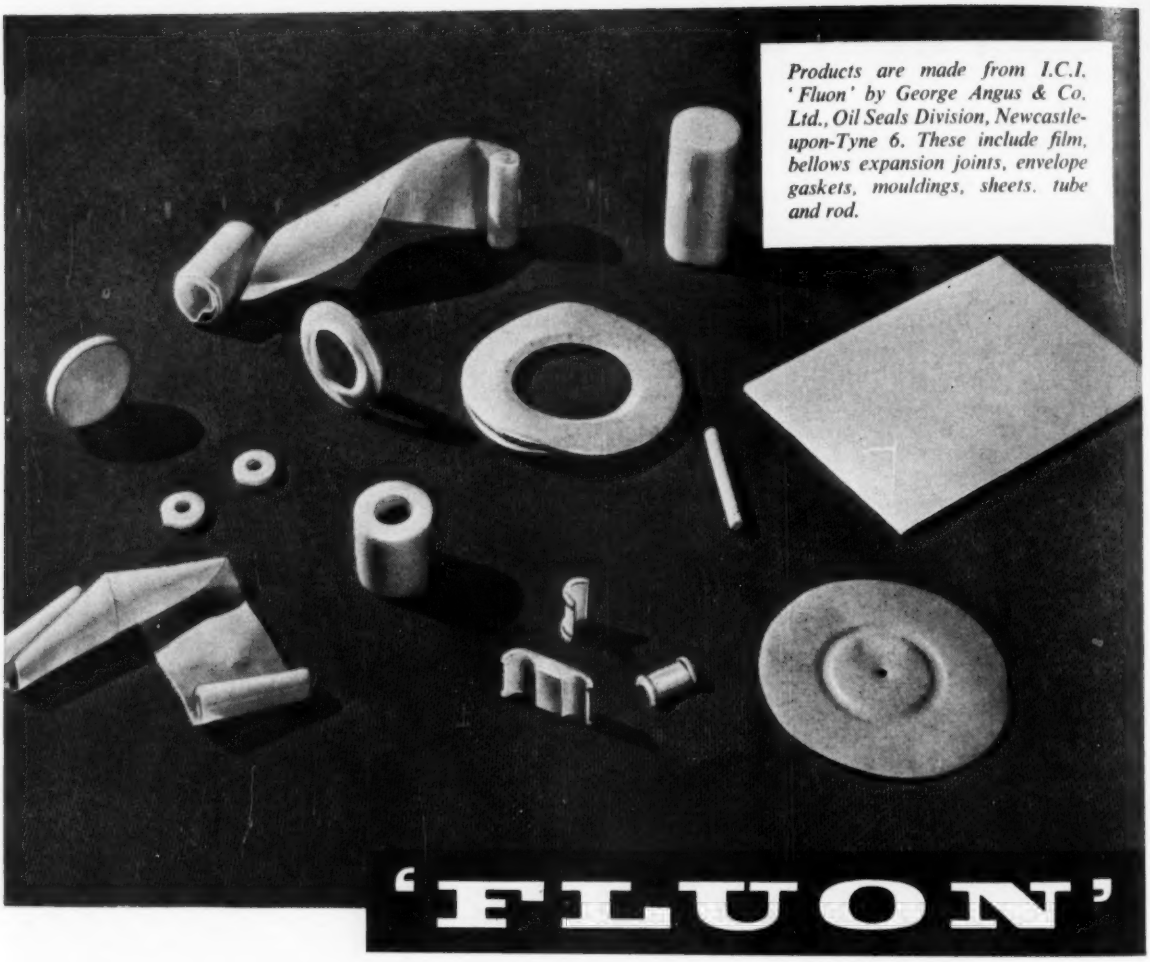
A list of leading Oil Companies using " Bitumastic " products is given with technical information in our Pipeline Data Booklet. Send for a copy today.

"BITUMASTIC"

BITUMASTIC

SPECIALISTS IN ANTI-CORROSIVE COATINGS
SPECIALISTS IN PIPELINE PROTECTION

H 133 WAILES DOVE BITUMASTIC LTD HEBBURN CO. DURHAM



Products are made from I.C.I. 'Fluon' by George Angus & Co. Ltd., Oil Seals Division, Newcastle-upon-Tyne 6. These include film, bellows expansion joints, envelope gaskets, mouldings, sheets, tube and rod.

OIL TIGHT SEALS AT ALL TEMPERATURES WITH 'FLUON' P.T.F.E.*

'FLUON' is completely unaffected by oil at all temperatures ever likely to be encountered in normal machines. It is also inert to all known chemicals except fluorine and molten alkali metal over the temperature range minus 80°C to 250°C. It has high mechanical strength and a very low coefficient of friction. Here is the perfect material for oil seals, gaskets and packings, where extremes of temperatures or special fluids are involved.

** 'Fluon' is the registered trade mark for *polytetrafluoroethylene manufactured by I.C.I.*

ICI

IMPERIAL CHEMICAL INDUSTRIES LTD., LONDON, S.W.1.

PF. 5

Atmospheric and Vacuum Distillation Units

Combined Distillation, Cracking, Reforming and Vapour Phase Treating Units

Pressure Distillate Re-run Units

Gasoline Recovery and Stabilization Units

Fractionating Columns and Tube Stills

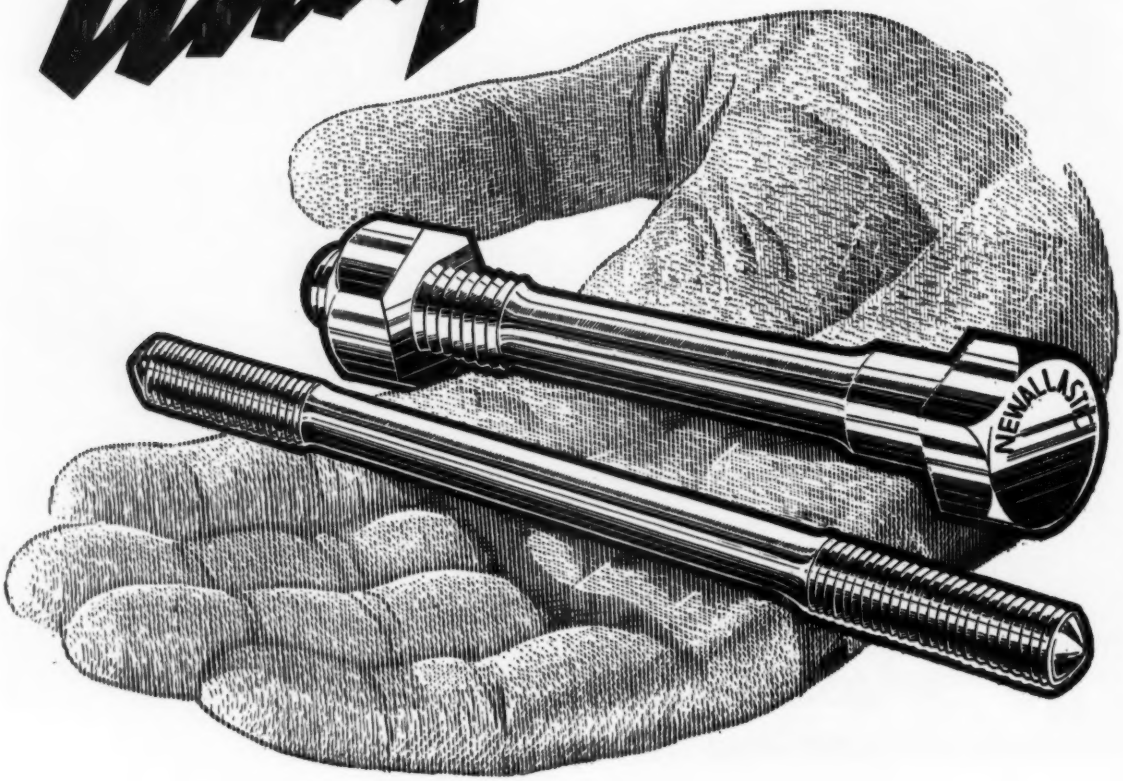
Wax Refining, Sweating and Moulding

A. F. CRAIG & COMPANY LIMITED

CALEDONIA ENGINEERING WORKS • **PAISLEY** • **SCOTLAND**

LONDON OFFICE: 727 SALISBURY HOUSE · LONDON WALL · E.C.2 · PHONE **NAT**IONAL **3964**

Unique

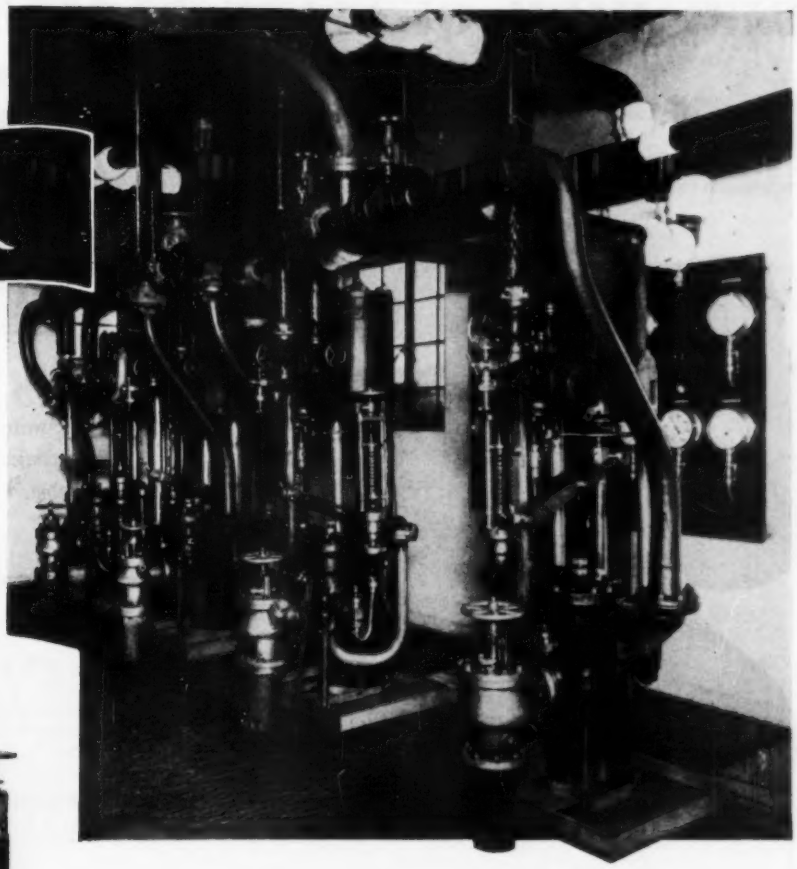


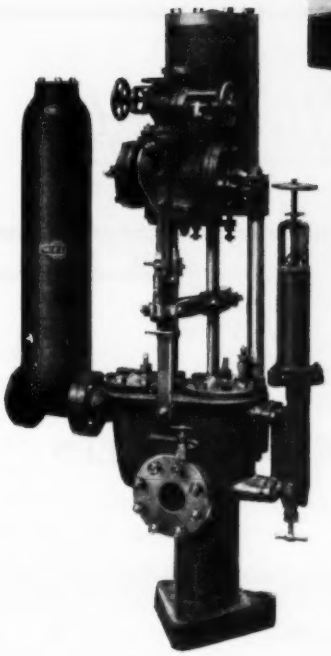
"Newallastic" bolts and studs have qualities which are absolutely unique. They have been tested by every known device, and have been proved to be stronger and more resistant to fatigue than bolts or studs made by the usual method.

C. P. Newall & Co., Ltd.

POSSILPARK GLASGOW · N

WEIR

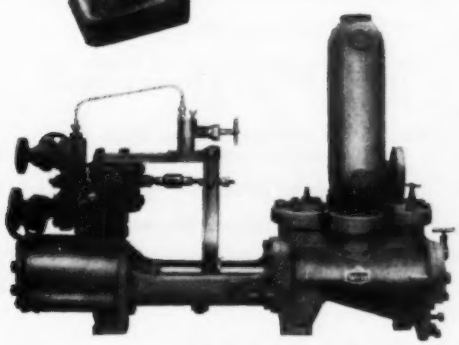




OIL FUEL PUMPS

Weir Oil Fuel Pressure Pumps are made in vertical and horizontal designs with single steam cylinder and double-acting oil end, and are specially suitable for pumping the heaviest and most viscous qualities of fuel oil. The Weir Piston Valve Chest ensures certainty of action and economical working.

Weir Oil Fuel Pressure and Transfer Pumps and Forced Lubrication Pumps are supplied in standard sizes and capacities.



G. & J. WEIR LTD.
CATHCART : GLASGOW

Weir Products include
FEED PUMPS · FEED HEATERS · FEED REGULATORS
EVAPORATING AND DISTILLING PLANTS
DE-AERATORS · ETC.

OUR HIGH QUALITY IS MAINTAINED...

IN ALL FITTINGS SUPPLIED TO REFINERY & CHEMICAL PLANTS

MILLENNIUM KEY

Please write for bulletins which give full technical information on each type of fitting.

Lake & Elliot Ltd.
BRAINTREE · ENGLAND

TELEPHONE · BRAINTREE 1491

HANDY VOLUMES OF THE ASTM/IP PETROLEUM MEASUREMENT TABLES

British and Metric Editions

	s.	d.		s.	d.
Vol. A. Interrelation of Units, Gravities and Density and Volumes	2	0	Vol. G. Reduction of Volume 60°F. against Specific Gravity 60/60°F.	5	0
Vol. B. Weights per Unit Volume and Volumes per Unit Weight against Sp. Gr. 60/60°F....	3	6	Vol. H. Miscellaneous Metric Tables ...	3	6
Vol. C. Reduction of Observed Specific Gravity and Volume to 60°F. For LPG and Casinghead Gasoline	5	0	Vol. I. Reduction of Observed Density and Volume to 15°C. For LPG and Casinghead Gasoline	6	0
Vol. D. For Aviation Gasoline, Motor Gasoline, Kerosine and Gas Oil	6	0	Vol. J. For Aviation Gasoline, Motor Gasoline, Kerosine and Gas Oil	6	6
Vol. E. For Diesel Fuel and Fuel Oils ...	6	6	Vol. K. For Diesel Fuel and Fuel Oils ...	7	6
Vol. F. For Fuel Oils and Bitumen	6	6	Vol. L. For Fuel Oils and Bitumen	7	6

British Tables A—G; Metric Tables H—L

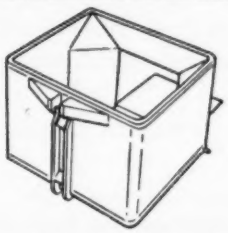
Obtainable from:—

INSTITUTE OF PETROLEUM
26, Portland Place, London, W.1.

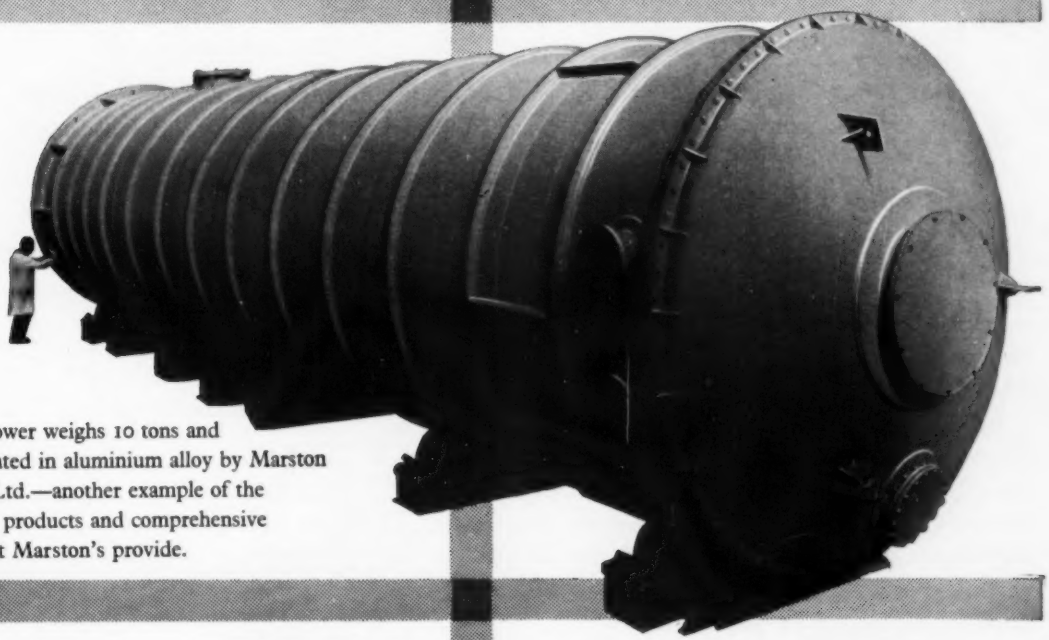
MARSTON EXCELSIOR *in the Service of Industry*

Marston's have unrivalled experience in the fabrication of light alloys—of all shapes and sizes. Their products have earned a reputation for efficiency and reliability that is world-wide.

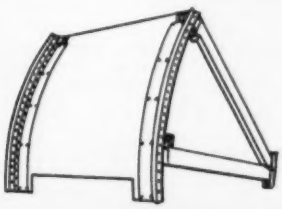
★ *Light Alloy Fabrication*
★ *Specialised Engineering Assemblies*
★ *Laminated Plastic Components*
★ *Flexible Tanks* ★ *Radiators and Heat Exchangers*



This truck-container is designed to carry granular material of particle size approximately $\frac{1}{16}$". Special attention had to be paid to the fit of the door and the smooth finish of the interior. The body ($\frac{3}{8}$" Plate Kynal M 39/2) was welded by the Argon arc and Argonaut processes.



This 52′ tower weighs 10 tons and was fabricated in aluminium alloy by Marston Excelsior Ltd.—another example of the specialised products and comprehensive service that Marston's provide.



This radial sluice-gate is 6′ 6″ wide and 6′ high. It is made of aluminium alloy, to minimise maintenance costs. To obtain a clean design free from any crevices where corrosion might start, the gate was welded by the Argon arc process. It is believed to be one of the first examples in this country of a radial sluice-gate in welded aluminium alloy.

MARSTON EXCELSIOR LIMITED

FORDHOUSES, WOLVERHAMPTON. Tel: Fordhouses 3361

(A subsidiary company of Imperial Chemical Industries Ltd.)

MAR 192

BY APPOINTMENT TO HER MAJESTY THE QUEEN
Suppliers of Fire Extinguishers The Pyrene Company Limited

Complete Fire Protection *for* Oil Refineries *and* Chemical Plants

Oil, in its many stages of processing—distillation, cracking, separation and refining—is a subject of constant study by Pyrene chemists and fire safety engineers. Through years of unrivalled experience we have evolved a complete range of modern fire fighting equipment to meet the various fire dangers that are always present in every branch of the oil industry. In the production of petroleum spirit, fuel and lubricating oils, bitumen, petroleum chemicals, alcohols and solvents, and in the increasingly wide uses of these products in industry, there are no fire problems beyond the scope of "Pyrene" Fire Protection.

Pyrene TRADE MARK FIRE PROTECTION

An investment in peace of mind

You should know about important "Pyrene" developments
Write Dept. J.P.

THE PYRENE COMPANY LIMITED

9 GROSVENOR GARDENS · LONDON S.W.1 *Tel. Victoria* 3401
Head Office & Works: BRENTFORD, MIDDLESEX. *Canadian Plant:* TORONTO

DRILLING AND PRODUCTION SAFETY CODE

(Loose Leaf)

Part 4 of Model Code of Safe Practice in the Petroleum Industry

Price 12s. 6d. post free

A 3-ring binder to hold this and three other codes can be supplied at the price of 15s. 6d.

Obtainable from

The Institute of Petroleum
Manson House, Portland Place, London, W.1

ADVERTISERS

Babcock & Wilcox Ltd.	xviii
Baker Oil Tools Inc.	xix
Birmingham Battery & Metal Co. Ltd.	July
British Ceca Co. Ltd.	Sept
Peter Brotherhood Ltd.	Sept
W. P. Butterfield Ltd.	Sept
A. F. Craig & Co. Ltd.	vii
Dorr-Oliver Co. Ltd.	Aug
Ferranti Ltd.	Apr
Foster Wheeler Ltd.	xx
Foxboro-Yoxall Ltd.	Sept
W. J. Fraser & Co. Ltd.	Sept
General Refractories Ltd.	xvii
Goodyear Tyre & Rubber Co. (Gt. Britain) Ltd.	Mar
Matthew Hall & Co. Ltd.	xiii
Hayward-Tyler & Co. Ltd.	June
Hughes Tool Co.	July
IBM United Kingdom Ltd.	Apr
Imperial Chemical Industries Ltd. (Metals Division)	xv
Imperial Chemical Industries Ltd. (Plastics Division)	vi
Kellogg International Corporation	iv
Richard Klinger Ltd.	i
Lake & Elliot Ltd.	x
A. & J. Main & Co. Ltd.	July
Marston Excelsior Ltd.	xi
Metropolitan-Vickers Electrical Co. Ltd.	Sept
A. P. Newall & Co. Ltd.	viii
Newman, Hender & Co. Ltd.	Sept
Power-Gas Corporation Ltd., The	iii
Procon (Gt. Britain) Ltd.	xvi
Pyrene Co. Ltd.	xii
Rubery, Owen & Co. Ltd.	June
Simmonds Aerocessories Ltd.	ii
Sir Isaac Pitman & Sons Ltd.	May
Sunvic Controls Ltd.	Feb
Universal Oil Products Co.	Sept
Wailes Dove Bitumastic Ltd.	v
G. & J. Weir Ltd.	ix
Henry Wiggin & Co. Ltd.	Inside back cover
Yorkshire Copper Works Ltd., The	Feb

THE

MATTHEW HALL

GROUP OF COMPANIES

MATTHEW HALL HOUSE, DORSET SQUARE, LONDON, N.W.1.

Durban
West Indies

Johannesburg
Salisbury (Central Africa)

Gateshead
Natal

Bolton

Manchester
Walkden

Bristol
Bolsover

Glasgow
Cape Town

TECHNICAL WORKS ON PETROLEUM

- JOURNAL OF THE INSTITUTE OF PETROLEUM
  Annual Subscription 94s. 6d.

- INSTITUTE OF PETROLEUM REVIEW
  Annual Subscription 15s. 0d.

- MODERN PETROLEUM TECHNOLOGY
  (2nd (1954) Edition)
  Price 35s. 0d. post free

- STANDARD METHODS FOR TESTING PETROLEUM AND ITS PRODUCTS
  Price 40s. 0d. post free

- REVIEWS OF PETROLEUM TECHNOLOGY VOL. 14
  (Covering 1952–1954)
  Price 35s. 0d. post free

- MOLECULAR SPECTROSCOPY
  Price 42s. 0d. post free

- PETROLEUM MEASUREMENT MANUAL
  Price 28s. 6d. post free

Published by

The Institute of Petroleum
26 Portland Place, London, W.1

bi-metal tubing

Specially made for Petroleum, Petrochemical and Heat Exchange Applications

I.C.I. copper alloy tubes, such as 'Alumbro' aluminium-brass and 'Kunifer' 30, are giving excellent service in many heat exchange applications in the petroleum and other industries.

In certain circumstances, a tube is needed which must show equally good resistance to different external and internal corrosive conditions.

To meet such requirements, I.C.I. Bi-metal Tubing is available in any combination of the Division's range of non-ferrous alloys and steel. A steel tube, for instance, can be supplied with an 'Alumbro' liner, or an 'Alumbro' tube with a steel liner and an 'Alumbro' ferrule.

If you have a problem involving dual corrosion, you should consider using

METALS DIVISION

BI-METAL TUBING

IMPERIAL CHEMICAL INDUSTRIES LIMITED, LONDON, S.W.1

M397

True satisfaction in building comes only with the finished job

Procon has just completed construction of this 20,000 bbls. per stream day UOP Fluid Catalytic Cracking Unit for Ashland Oil & Refining Company at Catlettsburg, Kentucky.

Here at Procon we take a lot of satisfaction in all phases of our work as builders. Everything we do, from designing and engineering through each stage of construction, gives us that feeling of accomplishment which is so rewarding a part of any job well done.

We only get our fullest measure of satisfaction, though, when the job is finished, faithfully done to every requirement of specification and time.

Procon's experienced organization plans and builds refineries, petrochemical and chemical plants anywhere in the free world. You can count on any project you trust to Procon being completed to your true measure of satisfaction, too.

PROCON (*Great Britain*) LIMITED
BUSH HOUSE, ALDWYCH, LONDON, W. C. 2, ENGLAND
PROCON INCORPORATED, DES PLAINES, ILLINOIS, U. S. A.
PROCON (CANADA) LIMITED, TORONTO 18, ONTARIO, CANADA
PROCON INTERNATIONAL S. A., SANTIAGO DE CUBA

WORLD-WIDE CONSTRUCTION FOR THE PETROLEUM, PETROCHEMICAL AND CHEMICAL INDUSTRIES

DURAX

GR

THE INDISPENSABLE REFRACTORY!

★ *RAMMING PATCHING & MONOLITHIC LININGS*

★ *SPECIAL & EMERGENCY SHAPES · COMPLETE LININGS*

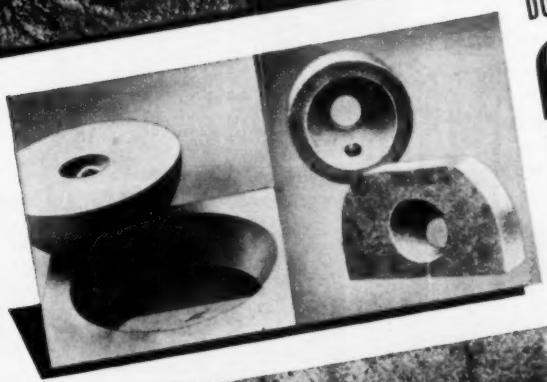
★ *THIN SOUND & STRONG JOINTING*

★ *PNEUMATIC GUN CEMENT LININGS*

DURAX No 1

PLASTIC FIREBRICK COMPOSITION

Supplied ready mixed for immediate use. Suitable for rammed linings and patching existing Durax No. 1 or firebrick linings. Service temperature range 1300/1650°C.



DURAX No 2

REFRACTORY CONCRETE

For casting in situ and making special shapes. Supplied dry. Special characteristics include—rapid setting as hard as firebrick: pours into position: no permanent volume change: little tendency to spall. Maximum service temperature 1300°C.

DURAX No 3

REFRACTORY CEMENT

A finely ground air setting cement for jointing all types of firebricks. Supplied dry. Special characteristics include—produces thin and strong joints: negligible shrinkage: highly refractory: economical in use. Maximum service temperature 1650°C.

DURAX No 5

GUNNING OR PLASTERING CEMENT

A cement designed for application with a pneumatic gun. Alternatively it may be plastered into position. Durax No. 5 has little rebound loss when applied by gun to Catalytic Regenerators and forms a dense tough lining with a maximum service temperature of 1300°C.

★ *Fully descriptive literature on all of these grades of Durax is available on request*

GENERAL REFRACTORIES LTD

GENEFAX HOUSE · SHEFFIELD 10 Telephone SHEFFIELD 31113

284

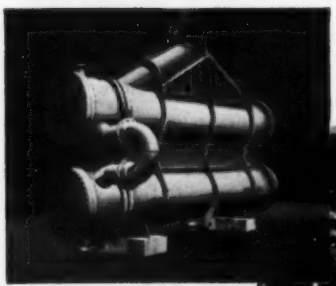
BABCOCK

Equipment for the Oil and Chemical Industries

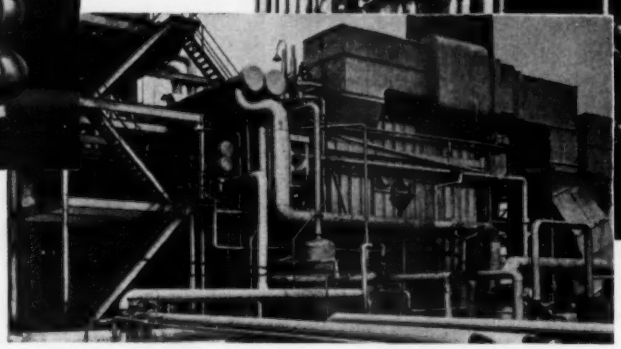
Babcock & Wilcox Ltd. is outstandingly well equipped in experience, techniques and manufacturing facilities to meet the demands of the oil and chemical industries for *complete steam-raising plants*, for *treating towers, manifolds* and other *pressure-vessels* in mild-steel or clad plate; and for *heat-exchangers, separately-fired superheaters* and plant for the *utilization of waste heat.*

It has developed techniques for welding high-alloy steels, which have been successfully applied to the manufacture of heat-exchangers operating at very high temperatures, or for use with corrosive working fluids.

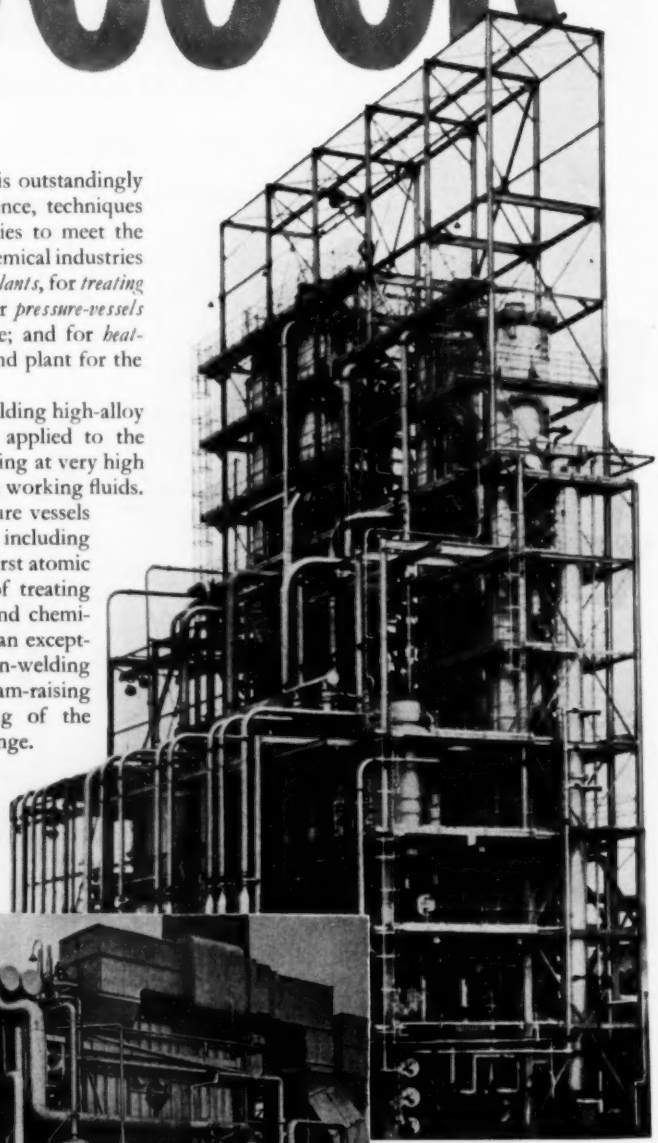
Many of the world's largest pressure vessels have been Babcock fusion-welded, including the giant heat-exchangers of Britain's first atomic power stations and a large number of treating towers for the world's oil refineries and chemical plants. The Company has, indeed, an exceptional experience of fabrication by fusion-welding and, as the world's largest maker of steam-raising plant, has a thorough understanding of the principles and problems of heat-exchange.



Heat-exchanger built by Babcock for service in an oil refinery.



One of a number of Babcock Integral-Furnace boilers, fired by refinery-gas and- or oil; in an "outdoor" type installation, at a large oil refinery.



Distillation unit at an oil refinery comprising Babcock fusion-welded columns.

BABCOCK & WILCOX LTD. BABCOCK HOUSE, 209 EUSTON RD. LONDON, N.W.I.

Here's what you can do with the **BAKER FULL-BORE RETRIEVABLE CEMENTER**

PERFORATE

FRACTURE ACIDIZE CEMENT

SWAB AND TEST

or use it with a **BAKER RETRIEVABLE BRIDGE PLUG** for as many straddle operations as required... in **ONE ROUND TRIP!**

A

Run tools in together

B

Release Plug, straddle interval, fracture or acidize

Swab and Test

C

Pick up plug, move to next interval

D

here's why it does these jobs better...

HOLDS HIGH PRESSURES FROM ABOVE OR BELOW Contains two sets of opposed "Rocker-Type Slips". Once packing element is packed off, pressure from above or below is automatically transferred through the proper set of slips to the casing.

FULL-BORE (Tubing I. D.) permits passage of instruments, or guns; prevents "screen-out" during fracturing operations.

Baker Full-Bore Retrievable Cementer Product No. 410

BAKER

OIL TOOLS, INC.

HOUSTON • LOS ANGELES • NEW YORK

Write for Catalog Supplements 319, 322, 323 for complete information on these products and their applications.

IRAQ GOVERNMENT LUBRICATING OIL REFINERY

Daura, Baghdad

In the extreme foreground are the cooling tower and blowdown facilities. Intermediate storage tankage is shown in the foreground.

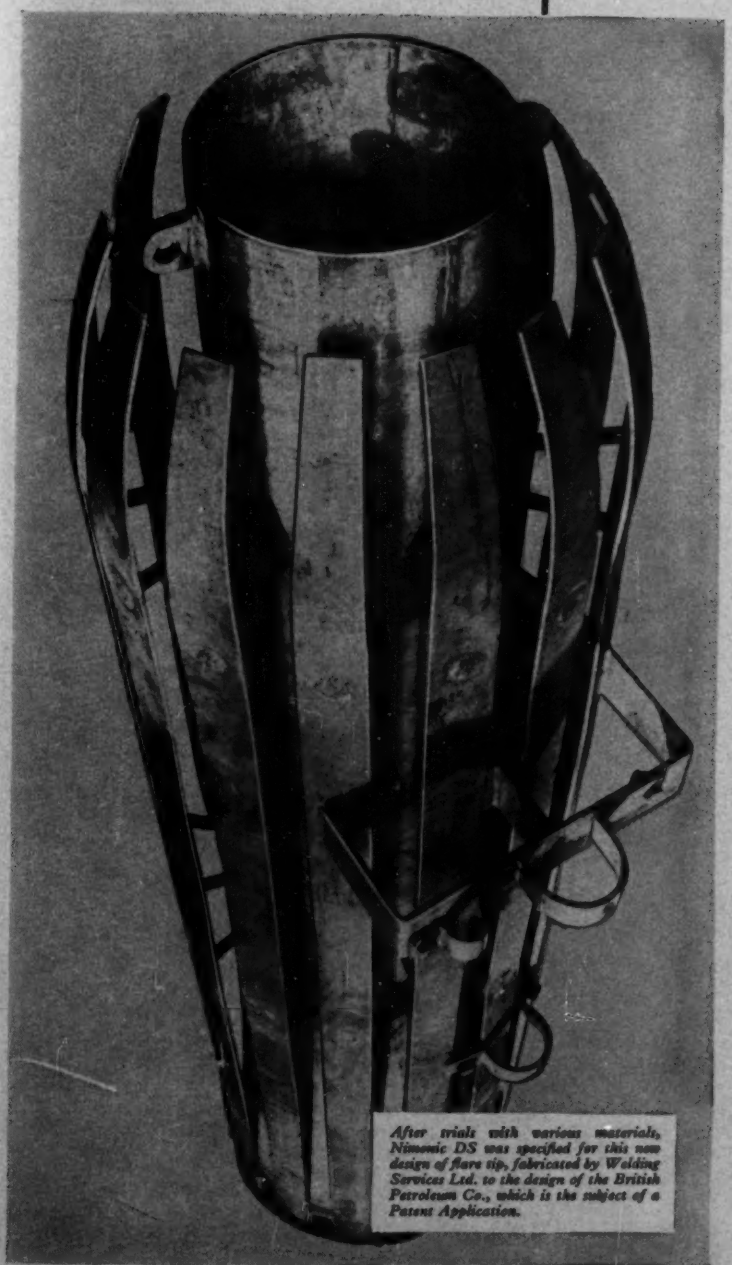
Process units, from right to left:—	*In the rear, from right to left:—*
Vacuum distillation unit	Blending tankage
Propane deasphalting and asphalt blowing units	Blending pump house with sub-station in front
Furfural treating unit	Can and drum making and filling plant
Propane dewaxing unit	
Clay percolation and acid treating units	Asphalt tankage and loading facilities

Designed and built by FOSTER WHEELER LIMITED

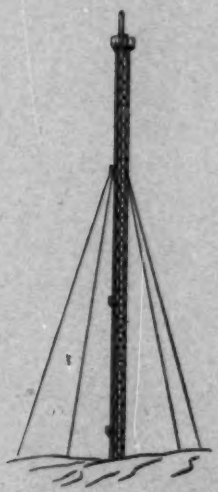
FOSTER WHEELER *London New York and Paris*

AT HIGH TEMPERATURES...

NIMONIC DS



After trials with various materials, Nimonic DS was specified for this new design of flare tip, fabricated by Welding Services Ltd. to the design of the British Petroleum Co., which is the subject of a Patent Application.



The flare stack is one of the items of plant that the oil refinery engineer would like to fit and forget. Unfortunately, the severe conditions at the tip where waste gases are burned present considerable difficulties which put a limit on life. The temperature of the flare tip varies with the volume of gases exhausted, their calorific value and the temperature and velocity of the prevailing wind. These conditions are aggravated by the tendency of the flame to sweep downwards around the outer lee side of the tip. From the fact that even from the ground it can be seen to be glowing red, it is believed that at times the temperature may reach 800°C. As a result of trials with various materials at the B.P. Group's Llandarcy refinery, Nimonic DS was selected for a new design of flare tip. This nickel-chromium alloy has good resistance to both oxidizing and reducing atmospheres and retains much of its strength at temperatures up to 960°C.

WIGGIN NICKEL ALLOYS

Full details of these flare stack tips are given in No. 42 of our technical publication, Wiggin Nickel Alloys. Please write for a free copy.

'Nimonic' is a Registered Trade Mark

HENRY WIGGIN & COMPANY LIMITED *WIGGIN STREET · BIRMINGHAM · 16*

PSA 10714